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Antiferromagnetism and Ferrimagnetism*

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ABSTRACT. The present position of our knowledge of antiferromagnetism, including ferrimagnetism, is reviewed, and some very interesting phenomena concerning the magnetic behaviour of certain ferrites and of pyrrhotite are described and explained.

I—ANTIFERROMAGNETISM

§1. THE NEGATIVE MOLECULAR FIELD AND ANTIPARALLEL SYSTEMS

We know that in his celebrated theory of ferromagnetism (Weiss 1907) represented the interactions between the magnetic moments of neighbouring atoms by means of a molecular field

$$H_{\mathrm{m}} = nJ \qquad \ldots\ldots(1)$$

proportional to the magnetization J, n being a constant. The magnetic susceptibility s of the substance is therefore given by the Curie–Weiss equation

$$s = C/(T - nC). \qquad \ldots\ldots(2)$$

The reciprocal of the susceptibility $1/s$ decreases linearly with absolute temperature and, when n is positive, becomes zero at a temperature $\theta = nC$, called the Curie temperature, or better the Weiss temperature, below which the substance is spontaneously magnetized under the action of its own molecular field: in this way one can account for the principal properties of ferromagnetic substances like iron, nickel, etc. When n is negative s takes a finite value at absolute zero equal to $-1/n$.

About 1932 I suggested (Néel 1932 a) that eqn. (2), which is based on the hypothesis of a random orientation of the atomic magnetic moments in the absence of an applied field, ought to break down at low temperatures because antiparallel arrangements of atomic moments should be formed under these conditions. In fact, the original crystalline lattice ought to break down into two sub-lattices A and B, with the moments of the atoms in A directed in one sense and those in B directed in the opposite sense, as shown in fig. 1. Energy considerations show that these two sub-lattices should be such that an atom in the sub-lattice A should have the maximum possible number of neighbours in sub-lattice B and vice versa: in fig. 1 all the neighbours of an atom A are of type B. Under the action of a field *h* this antiparallel arrangement is deformed (fig. 2).

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* Delivered in French; translated into English by Professor L. F. Bates.

An elementary calculation on classical lines, applied to elementary moments which are capable of being freely rotated, shows that when the temperature is markedly below $-nC$ the magnetic susceptibility of the system is constant, independent of the temperature, and given by

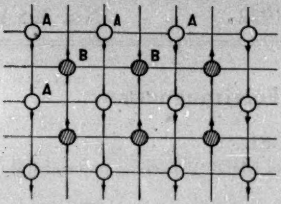

Fig. 1. Resolution of a plane lattice into two sub-lattices.

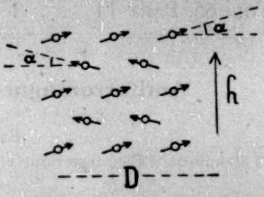

Fig. 2. Action of a field *h* on an antiparallel arrangement; the direction of antiferromagnetism is given by D.

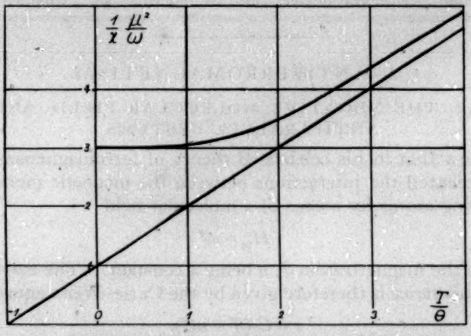

Fig. 3. Variation with temperature of the susceptibility of an antiparallel arrangement of moments; the asymptote corresponds to the Curie–Weiss law. *

$$s = -k/n, \qquad \ldots\ldots(3)$$

where *k* is a numerical coefficient equal, for example, to $\frac{1}{3}$ for a body-centred-cubic lattice or for the two-dimensional case represented in fig. 1. At high temperatures with respect to $-nC$ the antiparallel arrangement is destroyed and eqn. (2) is again obeyed. In conjunction with the properties of a diatomic arrangement one deduces that $1/s$ varies with T in the manner indicated by the curve of fig. 3: the asymptote of this curve corresponds to the Curie–Weiss law given by eqn. (2).

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* In diagrams for which blocks were already available χ and S are sometimes used to indicate susceptibility.

§2. THE INTERPRETATION OF THE MAGNETIC PROPERTIES OF MANGANESE AND CHROMIUM

The mechanism which has just been described gives at low temperatures something which may be conveniently termed *constant paramagnetism*. I proposed at the time (Néel 1932b) to explain on these lines the magnetic properties of manganese and chromium which, in effect, exhibit a constant paramagnetism too large to be explained by the Pauli theory of paramagnetism arising from free or partially free electrons. According to the point of view proposed here, one therefore attributes to the atoms of manganese or of chromium a definite magnetic moment. I estimated the value of nC to be 1720° K for manganese and 4150° K for chromium, so that the region of temperature at which measurements can be made is limited to that where the susceptibility is practically independent of temperature. Yet, on decreasing the interactions between the magnetic atoms, it should be possible to reach the region of the curve in fig. 3 which is close to the asymptote and to obtain direct evidence of the magnetic moments of the substances under consideration. By dissolving manganese or chromium in a non-magnetic metal like gold, silver or copper, I showed that one obtains solid solutions obeying the Curie–Weiss law: fig. 4 shows, for example, the experimental results for manganese dissolved in silver. With the aid of the Curie constant C thus obtained one finds for manganese or chromium an atomic moment a little less than 4 Bohr magnetons.

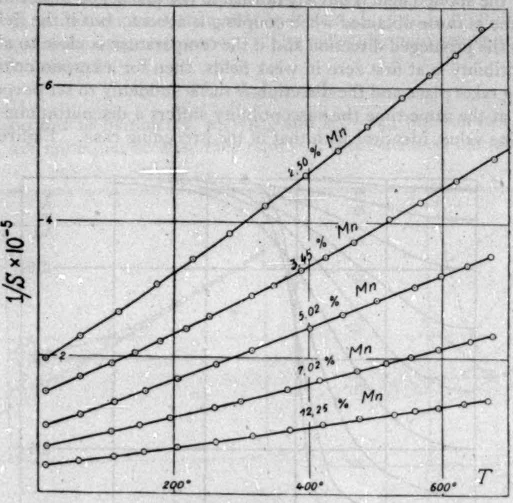


Fig. 4. Variation with temperature of the reciprocal of the susceptibility of solid solutions of manganese in silver.

§ 3. THE EFFECT OF MAGNETO-CRYSTALLINE COUPLING

A little later, in 1936, I examined (Néel 1936 a) the effect of magneto-crystalline coupling between the lattice and the atomic moments. Let us call *D* the common direction along which the atomic moments of the two sub-lattices are aligned at absolute zero, in one sense or the other; this may also be called the direction of antiferromagnetism. When the moments are not coupled with the lattice, that is to say where there exist only exchange forces of an isotropic kind, the direction *D* is orientated perpendicular to the applied field. When coupling exists *D* occupies a privileged direction and is fixed with respect to the lattice in the absence of an applied field, and remains orientated in this direction when the applied field is weak. If the applied field is already normal to the privileged direction the results are the same as those obtained when coupling is absent; but if the field is applied parallel to the privileged direction and if the temperature is close to absolute zero the susceptibility is at first zero in weak fields, then for a certain critical field H_0 decoupling takes place and the direction *D* turns suddenly to set perpendicular to the field: at the same time the susceptibility suffers a discontinuous change and takes a finite value, identical with that of the preceding case. Figure 5 gives the values of the susceptibilities for different directions of the field *H* with respect to the orientation of the privileged direction as a function of the reduced field H/H_0.

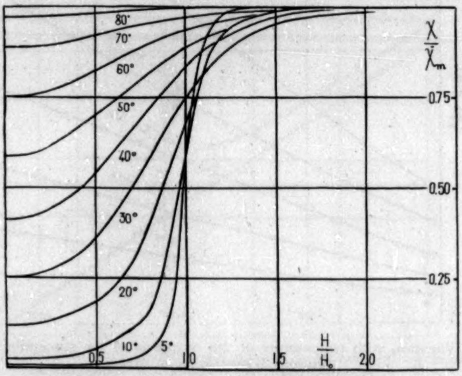


Fig. 5. Susceptibility as a function of field for different orientations of the field with respect to the direction of antiferromagnetism.

This phenomenon and its discontinuity have recently been observed by C. J. Gorter and his collaborators (Poulis *et al.* 1951, Poulis 1952) in the course of a study of the magnetic properties of a crystal of copper chloride ($CuCl_2.2H_2O$) at liquid helium temperatures.

When the directions *D* are randomly distributed, as is probably the case in a polycrystalline substance, one recognizes that the susceptibility must vary with the field: curve A of fig. 6 gives an example of the thermal variation of the susceptibility in weak fields and curve B that in strong fields. The theory of the phenomena of *D* coupling has recently been taken up in Japan by Nagamiya (1951) and his collaborators (Yosida 1952). It is possible that the hitherto unexplained variations of the magnetic susceptibility of platinum as a function of field and temperature, studied in detail by Collet and Foëx (1931) and Foëx (1939), have their origin in a similar mechanism.

§ 4. THE MOLECULAR FIELD APPLIED TO ANTIFERROMAGNETISM

The method proposed above only gives results applicable to the two extreme cases of very low or very high temperatures. In order to obtain a more precise idea of the phenomena in the intermediate region I proposed in 1936 (Néel 1936 b) to treat negative interactions by the method of the molecular field, considering the two sub-lattices A and B to be spontaneously magnetized, each in an inverse sense, under the action of two molecular fields $n_{aa}\mathbf{J}_a$ or $n_{bb}\mathbf{J}_b$, proportional to the magnetization $\mathbf{J}_a$ or $\mathbf{J}_b$, of its own sub-lattice and the other $n_{ab}\mathbf{J}_b$ or $n_{ba}\mathbf{J}_a$, proportional to the magnetization of the other sub-lattice. The molecular field acting on sub-lattice A will be, for example,

$$\mathbf{H}_a = n_{aa}\mathbf{J}_a + n_{ab}\mathbf{J}_b. \qquad \ldots\ldots(4)$$

Here, on account of symmetry, $n_{aa} = n_{bb}$ and $n_{ab} = n_{ba}$, but the two coefficients n_{aa} and n_{ab} are not equal because they represent short-distance interactions which are different. In addition, the coefficient n_{ab} is essentially negative, otherwise one would have ordinary ferromagnetism.

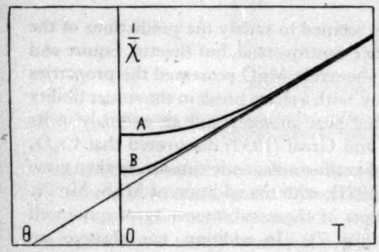


Fig. 6. Action of the field on the susceptibility of an antiferromagnetic arrangement: A, weak fields; B, strong fields.

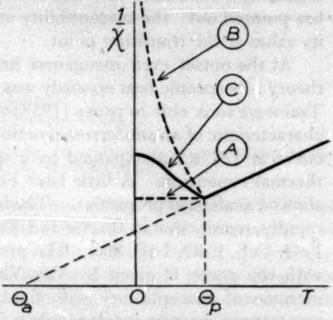


Fig. 7. Variation of the reciprocal of the susceptibility of an antiferromagnetic with temperature. A, the direction of antiferromagnetism is perpendicular to the applied field; B, parallel to the applied field; C, in any direction.

The analysis of the problem thus shows that the two sub-lattices acquire spontaneous magnetizations which are equal and opposite in sign and decrease with temperature to become zero at a definite temperature of transition T_a. In fact, at temperatures below T_a the magnetic moments are ranged in a regular manner, while above this temperature complete statistical disorder obtains in the substance. From an energy point of view this ordered phase behaves like an ordinary ferromagnetic, and is characterized by a specific heat anomaly of which the order of magnitude and type of thermal variation are the same as for a ferromagnetic substance.

As far as the magnetic properties are concerned, since the resultant spontaneous magnetization of the ordered phase is zero because the spontaneous magnetizations of the sub-lattices exactly compensate one another, the substance always remains paramagnetic whatever the temperature. The application of an external field perturbs the system and gives rise to a magnetic susceptibility which, in the absence of magnetocrystalline coupling with the lattice, remains *constant* up to the transition temperature T_a. Above this temperature the susceptibility obeys the Curie–Weiss law represented by eqn. (2) with a negative Curie point $\theta = nC$. On the whole the thermal variation of the susceptibility is represented by Curve A of fig. 7. One notes that the transition point (θ_p in the figure) is marked by a sharp change, that is to say by a discontinuity of the rate of change of susceptibility with respect to temperature. Such are the essential features of what it is now convenient to call *antiferromagnetism.*

When coupling exists between the atomic moments and the crystalline lattice the susceptibility always follows curve A when the applied field H is perpendicular to the direction of antiferromagnetism D, but, when the field H is parallel to this direction, Bitter has shown (1938) that one obtains a curve like B (fig. 7) with a susceptibility which disappears at absolute zero. Finally, with the directions D randomly distributed, one ought to observe a mean curve C, as Van Vleck (1941) has pointed out: the susceptibility at absolute zero is thus equal to two-thirds of its value at the transition point.

At the outset even manganese hardly seemed to satisfy the predictions of the theory: its specific heat anomaly was rather controversial, but Bizette, Squire and Tsaï were soon able to prove (1938) that the oxide MnO possessed the properties characteristic of an antiferromagnetic body, with a sharp break in the susceptibility curve at 122° K accompanied by a specific heat anomaly and an anomaly in its thermal expansion. A little later Foëx and Graaf (1939) discovered that Cr_2O_3 showed analogous properties. The list of antiferromagnetic substances then grew rapidly, mainly due to Bizette and Tsaï (1951), with the addition of MnS, MnTe, FeO, FeS, CoO, NiO, etc. The properties of these substances agree quite well with the curve C given by Van Vleck (fig. 7). In addition, one observes an increase of susceptibility with field, below the transition temperature, which represents a progressive decoupling for the direction D, predicted by the original theory.

Yet the most satisfactory confirmation of the fundamental ideas was really given by Shull. The theory of antiferromagnetism is based in effect on the breakdown of the crystalline lattice into two sub-lattices magnetized in opposite senses. If atoms possessing magnetic moments directed in opposite senses may be considered different from one another, then we have to deal with a kind of superlattice; such a superlattice cannot be revealed by means of X-rays whose diffraction is not affected by the orientation of the moments, but one can show it to exist by using a beam of neutrons, when extra diffraction lines are obtained which are characteristic of the antiferromagnetic state and which disappear when the temperature of the substance is raised above the transition temperature. Shull *et al.* (1951 b) should be given the credit for the experiments which permit us to fill in details of the antiferromagnetic structure. Figure 8, due to these authors, allows us to compare the diffraction diagrams of MnO above and below the transition point. One observes from the (111) plane the extra diffraction lines due to the magnetic superlattice. These experiments have shown that the atoms of manganese are arranged in successive planes perpendicular to a ternary axis and that these planes are magnetized alternately in opposite senses: now this is exactly the structure which I was led to propose some time ago (Néel 1948) from purely magnetic considerations. Neutron diffraction experiments also permit us to fix *D* the direction of antiferromagnetism. This is parallel to a quaternary axis for the cases of MnO, MnS, MnTe, CoO and NiO, while it is parallel to a ternary axis in FeO.

§ 5. PROPERTIES OF SOME ANTIFERROMAGNETIC CRYSTALS

In the case of a single crystal the relations between the axis of symmetry of the crystalline lattice and the direction *D* can be studied by purely magnetic methods. Let us take for example manganese difluoride MnF_2, which is a tetragonal uniaxial crystal of the rutile type. From the measurements of Bizette and Tsaï (1939) on powdered specimens, and of Stout and Griffel (1949) on the single crystal, it is seen that in the antiferromagnetic region the susceptibility remains practically independent of temperature when it is measured in a direction perpendicular to the quaternary axis, which corresponds to curve A of fig. 7, whilst it tends to become zero at 0° K after the manner of curve C along the direction of the axis: these are the properties which one would expect when the antiferromagnetic direction coincides with the quaternary axis. The rhombic sesquioxide of iron αFe_2O_3 is equally interesting: it exhibits a fundamental antiferromagnetism superimposed upon a very weak ferromagnetism whose origin is not very clear (Néel 1949) but which we may neglect here. The study of its magnetic properties suggested to me (Néel 1948, 1949) that at ordinary temperatures the successive layers of iron atoms, perpendicular to the ternary axis, were magnetized consecutively in opposite directions, with a direction of antiferromagnetism perpendicular to the ternary axis. These two predictions were confirmed by Shull *et al.* (1951 b) by means of neutron diffraction.

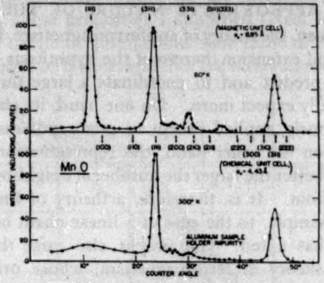


Fig. 8. Diffraction of neutrons by MnO (C. G. Shull). One notes the extra peak due to the antiferromagnetic resolution into two sub-lattices.

As has been shown by Morin (1950) and by Guillaud (1951) by magnetic studies, the sesquioxide of iron exhibits an anomaly at a temperature of −78° C. M. Pauthenet has undertaken the study of this question in my laboratory using a single crystal of haematite. The results (Néel and Pauthenet 1952) were roughly as follows: in a direction perpendicular to the ternary axis the susceptibility remains practically constant from liquid air temperatures up to the transition temperature 675° C. On the other hand, in the direction of the axis the susceptibility is at first very weak at low temperatures, taking a value in the region of $-78°$ C almost equal to the value along the perpendicular direction and maintaining that value up to the transition point. These facts may be explained very easily if one supposes that the direction of antiferromagnetism coincides with the ternary axis below $-78°$ C and moves into the perpendicular plane, *with freedom of orientation*, at higher temperatures. This change in orientation may be likened to those undergone by the directions of easy magnetization in uniaxial ferromagnetic bodies like cobalt or MnBi. It is to be noted that in the case of the latter substance Guillaud (1943) has shown that there exists a plane of easy magnetization perpendicular to the hexagonal axis below 84° K, whilst the hexagonal axis becomes an axis of easy magnetization above that temperature.

§ 6. THE APPROXIMATE NATURE OF THE THEORY

As we have just seen, the theory of antiferromagnetism, based on the reduction to two sub-lattices and extension thereto of the hypothesis of the molecular field, has permitted us to predict and to coordinate a large number of experimental facts: one could hardly expect more. On one hand, its classical nature does not allow it to be rigorously applied except to atoms possessing a relatively large magnetic moment; on the other hand, the representation of interactions by a molecular field is the better the larger the number of neighbours which act magnetically upon a given atom. It is, therefore, a theory of limited application very badly adapted, for example, to the case of a linear chain of atoms, of spin $s=\frac{1}{2}$, as Kramers (1952) has noted. One might also raise the same objections to the molecular field theory of ferromagnetism, whose utility one nevertheless appreciates: it is only necessary to bear in mind the limited and approximate nature of the theory which one uses.

II—FERRIMAGNETISM

§ 1. IMPERFECT ANTIFERROMAGNETISM

In an antiferromagnetic substance the two sub-lattices are physically and essentially identical, so that their spontaneous magnetizations compensate one another exactly, and the resultant spontaneous magnetization is consequently exactly zero. But one could very well imagine, for some reason or other, that the two sub-lattices are not exactly equivalent; the spontaneous magnetization of one of the sub-lattices will then be greater than that of the other, and the resultant spontaneous magnetization will be different from zero, as in a ferromagnetic substance. This is the reason why the iron sulphide FeS is a normal antiferromagnetic, where the number of atoms of sulphur is equal to the number of atoms of iron, for the two sub-lattices are then exactly the same. But when there is a net excess of sulphur, as in the case of pyrrhotite $FeS_{1.17}$, the two sub-lattices are different and ferromagnetism is exhibited: we will return to this example later. It is probable that the small superimposed ferromagnetism of αFe_2O_3 arises in an analogous manner.

However, the outstanding example of these phenomena is that of the ferrites Fe_2O_3MO, where M is a bivalent metal, such as copper, nickel, cobalt, iron, manganese, etc. The crystalline lattice is then of the spinel type Al_2O_3MgO. The metallic ions may occupy two different categories of sites from the crystallographic point of view: A sites surrounded by four atoms of oxygen and B sites surrounded by six atoms of oxygen. For each molecule there are one A site and two B sites. Verwey (Verwey and Heilmann 1947, Verwey and de Boer 1936) showed by x-ray studies that the ferromagnetic ferrites which are of interest to us possess a structure which is called *inverse,* in which the A site is occupied by a Fe^{3+} ion and the two B sites by the M^{2+} ion and the other Fe^{3+} ion. Experiment shows that magnetically these substances are characterized by a feeble saturation magnetization with respect to the total magnetic moment of the ions which are present, and above the Curie point by a thermal variation of the susceptibility which is distinctly different from that of ordinary ferromagnetics; by representing the reciprocal of the susceptibility $1/\chi$ as a function of the temperature T one obtains a hyperbola instead of a straight line, as is evident in the early measurements of Mlle Serres (1932) and the more recent results of Fallot and Maroni (1951) (cf. fig. 12). This was an irritating puzzle for the theoreticians.

In order to interpret these properties I supposed (Néel 1948) that in these substances the principal magnetic interactions were those of the ions situated in A sites with the ions situated in B sites, and that the interactions AB were *negative*.

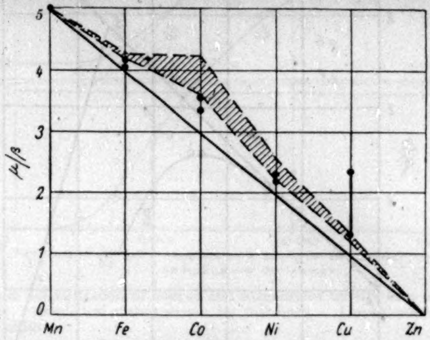


Fig. 9. Comparison of molecular moments predicted by theory and experimental values for certain ferrites.

One may easily show that if the interactions AB are sufficiently large with respect to the interactions AA between atoms situated in A sites and the interactions BB between atoms situated in B sites, two magnetic sub-lattices are formed, composed of the ions situated in sites A and of the ions situated in sites B respectively: these two sub-lattices are both magnetized to saturation at absolute zero, but in *opposite senses*. As these two sub-lattices are essentially different, there exists a resultant spontaneous magnetization which is not zero and a ferromagnetism which arises, paradoxically enough, from negative interactions. In view of this fact and of the rather special properties which follow from it, I thought it appropriate to give the name *ferrimagnetism* to this mechanism.

§2. PROOFS OF FERRIMAGNETISM

It follows from the above hypothesis that at low temperatures the magnetic moments of the two ferric ions in the molecule compensate one another because they belong to different sub-lattices: the molecular moment is therefore merely equal to that of the ion M^{2+}. Figure 9 gives in Bohr magnetons the saturation molecular moments of a number of ferrites (black circles) from determinations made in different laboratories. The hatched region corresponds to the predicted theoretical moments, taking account of probable orbital moments; the continuous line refers to moments due to spin only. The agreement is very satisfactory except in the case of copper: we shall see later a reason for this apparent exception.

Neutron diffraction has brought an even more direct confirmation of the ferrimagnetic structure: Shull *et al.* (1951 a) has shown that in the case of magnetite the ions situated in A sites possess magnetic moments oppositely directed to the resultant total magnetization.

Another striking confirmation of the theory is given by the variation with concentration of the molecular moment of certain mixed ferrites in which a portion of the ions M is replaced by non-magnetic Zn^{2+} ions. For zinc ferrite is a *normal* ferrite, i.e. a ferrite in which the two Fe^{3+} ions are in the two B sites, whilst the Zn^{2+} ion occupies the A site, for which it has a special affinity. When in an inverse ferrite one replaces an M ion in a B site by a Zn ion, that Zn ion goes into an A site causing the movement of an Fe^{3+} ion from a B to an A site. This results in the reversal of the magnetic moment of this Fe^{3+} ion, which is equal to five Bohr magnetons. The net effect is that the replacement of an M ion by a Zn ion produces an increase of moment equal to $10-m$ Bohr magnetons, m denoting the moment of the M ion. These predictions were verified in a remarkable manner by the experiments of E. W. Gorter (1950) at Eindhoven and by Guillaud (1949) at Bellevue. Figure 10 shows as an example the results obtained with mixed ferrites of nickel and zinc: on the NiO side the experimental moments fall remarkably well upon the theoretical line AB.

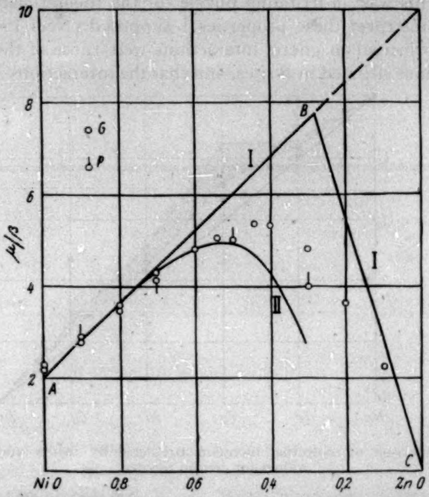


Fig. 10. Comparison of molecular moments predicted by theory and the experimental values for the series of mixed ferrites of nickel and zinc: G, Guillaud's values; P, Gorter's values.

The case of copper ferrite, to which we have just referred, is particularly interesting: here we have an inverse ferrite in which the affinity of the M ion, namely the Cu^{2+} ion, for the B sites is particularly weak. It therefore happens that at high temperatures these ions are randomly distributed over the A and B sites: on the average one-third are on the A sites and two-thirds on the B sites. When the temperature is lowered they all progressively reoccupy the B sites. Quenching permits us to keep in unstable equilibrium the different intermediate states and, therefore, makes manifest the variations of molecular moment as a function of the quenching temperature. Pauthenet and Bochirol (1951) have studied this phenomenon in my laboratory and have shown that the observed moments agree well with the moments predicted by the statistical theory. In fig. 11 the observed values are compared with the theoretical curves (full lines) in the case of copper ferrite and the closely analogous magnesium ferrite. These atomic migrations within the crystalline lattice, thus demonstrated by magnetic methods, have been confirmed by X-ray analysis by one of my collaborators, M. Bertaut (1951).

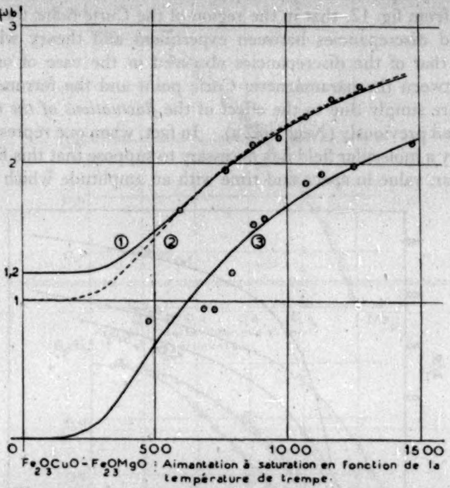


Fig. 11. Saturation magnetization of copper and magnesium ferrites as a function of quenching temperature; theoretical curves shown by full lines. Upper curve Fe_2O_3CuO; lower curve Fe_2O_3MgO.

In conclusion, we see that it is possible to predict the molecular moment of ferrimagnetic bodies with much greater exactness than that of the ordinary ferromagnetics, iron, nickel or cobalt. This was *a priori* very unexpected.

§3. APPLICATION OF THE MOLECULAR FIELD THEORY TO FERRIMAGNETISM

We have thus been able to extend the theory of ferrimagnetism by generalizing the hypothesis of the molecular field and by representing the different interactions present, AA, AB and BB, by three molecular field coefficients. We thus show that the susceptibility s above the Curie point is represented by a hyperbolic type of expression of the form

$$1/s = T/C + 1/\chi_0 - \sigma/(T-\theta), \qquad \ldots\ldots(5)$$

where C is the Curie constant corresponding to the given ions in the absence of interactions, and χ_0, σ and θ are functions of the three molecular field coefficients n_{AA}, n_{AB} and n_{BB}. Fallot and Maroni have shown that the susceptibility of ferrites can be effectively represented by an expression of the form (5). We merely note, as is obvious from fig. 12, that in the region of the Curie point there occur some rather marked discrepancies between experiment and theory whose origin is analogous to that of the discrepancies observed in the case of ordinary ferromagnetics between the paramagnetic Curie point and the ferromagnetic Curie point: they are simply due to the effect of the *fluctuations of the molecular field* which I studied previously (Néel 1932 a). In fact, when one represents magnetic interactions by a molecular field it is necessary to suppose that this field fluctuates about the mean value in space and time with an amplitude which is the greater the smaller the number of neighbouring atoms reacting with one another. Consequently, the disappearance of the ordered state takes place at a temperature a little lower (20° to 50° c) than the theoretical temperature corresponding to a molecular field which does not fluctuate.

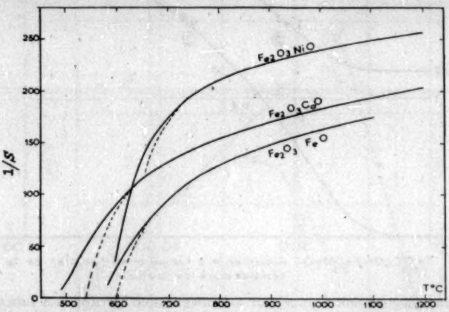
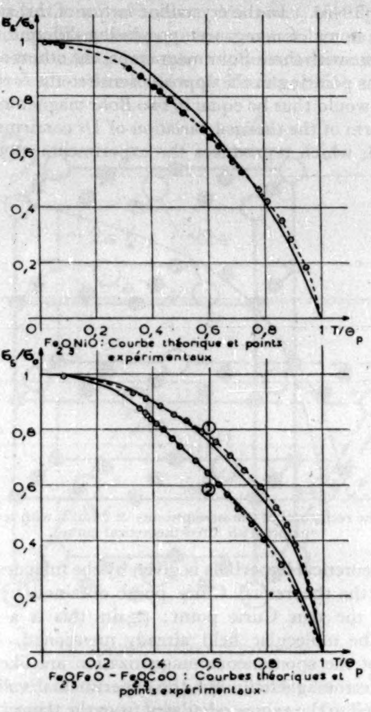


Fig. 12. Experimental values (full lines) of the reciprocal of the susceptibility of the ferrites of nickel, cobalt and iron as functions of temperature. The theoretical hyperbolae are shown by the broken lines.

The study of paramagnetic properties above the Curie point thus provides values of the three coefficients of the molecular field which, with the values of the moments of the ions, are sufficient to specify completely, to a first approximation, a ferromagnetic ferrite; one can thus calculate the curve of the thermal variation of the spontaneous magnetization without recourse to any other data. The comparison of these curves with the experimental curves provides a proof of the value of the method of the molecular field applied to ferrimagnetism. Figure 13, taken from a work by Pauthenet and Bochirol (1951), allows us to compare the experimental values of the spontaneous magnetization with the theoretical curves for the three ferrites of iron, cobalt and nickel. The agreement is very satisfactory. We notice that these curves appear very different from the corresponding curves for ferromagnetics, being in general more flattened than these.

§ 4. FEATURES OF FERRIMAGNETISM

One must emphasize that ferrimagnetism is essentially associated with a paramagnetic law of the hyperbolic form (eqn. (5)); the hyperbola may, of course, degenerate into its asymptotes. In order to conclude from the examination of the experimental data that ferrimagnetism rather than ferromagnetism exists, it is therefore necessary that the variation of the susceptibility with temperature above the Curie point should be of the form (5). But quite recently Zener (1952) proposed a breakdown of the iron lattice into two simple cubic sub-lattices, one composed of Fe^{3+} ions of five Bohr magnetons, the other of Fe^{-} ions of one Bohr magneton, the latter being orientated in the opposite sense to the former: the iron would then be a ferrimagnetic. Independently of the objections based on energy considerations which such a conception would raise, if it were true one should find



Top diagram: Fe_2O_3NiO.
Bottom diagram: (1) Fe_2O_3FeO; (2) Fe_2O_3CoO.

Fig. 13. Spontaneous magnetization of the ferrites of nickel, cobalt and iron as a function of the reduced temperature; experimental points and theoretical curves calculated from paramagnetic data.

above the Curie point a hyperbolic variation of the reciprocal of the susceptibility, $1/s$. In practice one actually finds the ordinary Curie–Weiss law. It therefore does not seem possible to accept Zener's point of view.

§ 5. OTHER FERRIMAGNETIC SUBSTANCES

Many other ferrimagnetic substances are recognized today in addition to the ferrites, for example, the antimonide of manganese, Mn_2Sb, studied at low temperatures by Guillaud (1943). In the crystalline lattice of this substance there are in effect two kinds of atoms of manganese possessing different electron structures: some are in a $3d^7$ state with three Bohr magnetons, the others are in a $3d^5$ state with five Bohr magnetons pointing in the opposite sense to the former: the theoretical molecular moment would thus be equal to two Bohr magnetons, whilst experiment gives 1·87. The form of the thermal variation of $1/s$ confirms this interpretation, as shown in fig. 14, which reproduces the experimental points of Mlle Serres (1947), while the theoretical hyperbola is given by the full curve. One notices the difference between the theoretical Curie point obtained by extrapolation from the hyperbola and the true Curie point: again this is a result of the effect of fluctuations of the molecular field already mentioned. The curves of the thermal variation of the spontaneous magnetization are likewise different from those of ordinary ferromagnetics: but the experimental values on the contrary approximate very well to the values calculated from the theory of ferrimagnetism if we use the values of the coefficients deduced from the study of paramagnetism (Néel 1948).

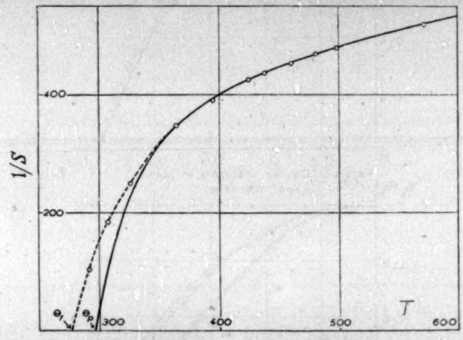


Fig. 14. Variation of the reciprocal of the susceptibility of Mn_2Sb with temperature (experimental points with fitted theoretical curve).

Another good example, of more interest, is that of the sulphides of iron. The sulphide of iron FeS in stoichiometric proportions is an antiferromagnetic substance with a transition point at 325° c. It belongs to the Ewald type B8, like NiAs. Let us number consecutively the planes of iron atoms perpendicular to the ternary axis; we may then imagine that one of the sub-lattices is formed by the planes of even order and that the other is formed by the planes of odd order.

For the non-stoichiometric sulphides the magnetic properties change gradually as the proportion of sulphur increases, and for the compound $FeS_{1\cdot09\,\text{approx}}$

ferromagnetic properties appear. In particular, the saturation magnetization seems to pass through a maximum in the region of the composition $FeS_{1\cdot 14}$, which is approximately Fe_7S_8: one is reminded of pyrrhotite. The saturation magnetization of pyrrhotite is small, and of the order of 0·36 Bohr magnetons per atom of iron: it is reasonable to suppose that we have here a case of ferrimagnetism due to lack of equality between the two sub-lattices, which were originally the same in FeS. This inequality should probably be associated with the unequal proportion of atoms of iron and sulphur in pyrrhotite. Moreover, as sulphur must always remain bivalent, the composition FeS_{1+x} must necessarily contain $1-2x$ of Fe^{2+} ions and $2x$ of Fe^{3+} ions. Also, one may suppose, on one hand with Hirone and Tsuya (1951) and on the other hand with Yosida (1951), that the ferric ions collect on the iron planes of even order perpendicular to the ternary axis, and that the planes of odd order contain only ferrous ions. In this way one obtains the necessary lack of symmetry and the correct order of magnitude for the saturation moment.

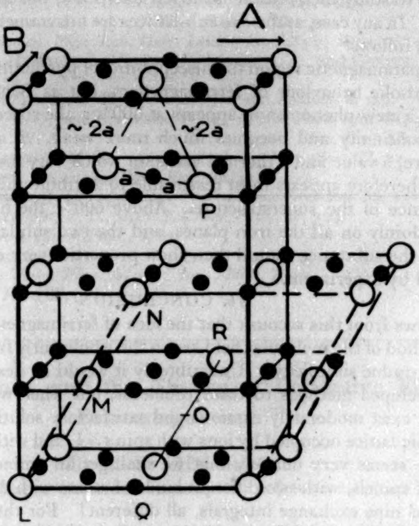


Fig. 15. Lattice structure of pyrrhotite.

Unfortunately, this explanation is not very satisfactory, for it neglects one essential fact: the crystalline lattice of FeS_{1+x} must be an incomplete lattice with x unoccupied places which are normally occupied by Fe^{2+} ions in FeS. I therefore think that these vacancies, or holes, must arrange themselves regularly on iron planes of even order and give rise to the required lack of symmetry. If this idea is correct, this lack of symmetry must correspond to a kind of superstructure discernible by x-rays, because the scattering powers of the holes and of the iron ions are different. I therefore asked M. Bertaut, the x-ray specialist in my laboratory, to find if pyrrhotite actually had the structure of NiAs and if the diffraction pattern did not contain by accident some supplementary lines. By making exposures which were sufficiently prolonged, Bertaut (1952) has actually found 240 diffraction spots which may be attributed to this superstructure and which indicate an ordered distribution of the holes: consequently it appears that this is the first known example of a structure containing holes in ordered arrangement. Figure 15 shows the structure obtained, corresponding to the formula Fe_7S_8T, where T is a hole. This figure shows the arrangement of the iron atoms and the holes in the planes of odd order. For the sake of clarity, planes of iron of even order, which contain no holes, have not been depicted, neither have the intermediary planes of sulphur. One of the sub-lattices is therefore probably formed by the planes of iron with holes, the other by planes without holes. One would like to study the position of the ferric ions, but this is not possible by x-ray methods. In any case, as the two sub-lattices are unsymmetrical, ferromagnetism necessarily follows.

In the paramagnetic region the susceptibility of pyrrhotite shows the characteristic hyperbolic behaviour of ferrimagnetism, but as Benoît (1952) showed at Grenoble, a new phenomenon appears at 600° c: the susceptibility undergoes a sharp discontinuity and becomes much more weak. It possesses, above this temperature, a value and a thermal variation which very much resemble those of FeS. It therefore appears most reasonable to attribute this discontinuity to the disappearance of the superstructure. Above 600° c the holes distribute themselves randomly on all the iron planes, and the two sub-lattices should become identical; the substance should then show properties very close to those of FeS, as is found by experiment.

§6. CONCLUSION

It follows from this account that the idea of ferrimagnetism and its treatment by the method of the molecular field are on the whole fairly fruitful in spite of their somewhat undue simplicity. Undoubtedly it would be desirable to apply more highly developed methods to these problems, but when we consider that there do not yet exist moderately rigorous and satisfactory solutions for the case of a simple cubic lattice occupied by ions with spin $s=\frac{1}{2}$, and with one single exchange integral, it seems very unlikely that we shall get an immediate solution of the problem of spinels, with two different kinds of atoms with different spins, greater than $\frac{1}{2}$, and nine exchange integrals, all different! For the time being it is not unwise to use a simple method even if it is a little rough and ready.

Finally, let us note that the studies of magnetic properties of antiferromagnetic and ferrimagnetic substances have enabled us, from the experimental data, to prove the necessary existence between magnetic atoms of indirect exchange interactions in which an intermediary, non-magnetic atom plays an essential part; there exists in this way magnetic coupling by the intermediary action of atoms of sulphur or of oxygen of the type Fe–O–Fe, Mn–O–Mn, Fe–S–Fe, etc. This is the superexchange whose possibility Kramers (1934) previously envisaged on theoretical grounds.

REFERENCES

Benoît, R., 1952, *C. R. Acad. Sci., Paris* **234**, 2174.
Bertaut, F., 1951, *J. Phys. Radium*, **12**, 252; 1952, *C. R. Acad. Sci., Paris*, **234**, 1295.
Bitter, F., 1938, *Phys. Rev.*, **54**, 79.
Bizette, H., 1951, *J. Phys. Radium*, **12**, 161.
Bizette, H., Squire, C. F., and Tsaï, B., 1938, *C. R. Acad. Sci., Paris*, **207**, 449.
Bizette, H., and Tsaï, B., 1939, *C. R. Acad. Sci., Paris*, **209**, 205.

COLLET, P., and FOËX, G., 1931, *J. Phys. Radium*, **2**, 290.
FALLOT, M., and MARONI, P., 1951, *J. Phys. Radium*, **12**, 256.
FOËX, G., 1939, *Congrès de Magnétisme de Strasbourg*, **3**, 187.
FOËX, G., and GRAAF, S., 1939, *C. R. Acad. Sci., Paris*, **209**, 106.
GORTER, E. W., 1950, *C. R. Acad. Sci., Paris*, **230**, 192.
GUILLAUD, C., 1943, *Thesis*, Strasbourg; 1949, *C. R. Acad. Sci., Paris*, **229**, 1133; 1951, *J. Phys. Radium*, **12**, 489.
HIRONE, T., and TSUYA, N., 1951, *Phys. Rev.*, **83**, 1063.
KRAMERS, H. A., 1934, *Physica*, **1**, 182; 1952, *Ibid.*, **18**, 101.
MORIN, F. J., 1950, *Phys. Rev.*, **78**, 819.
NAGAMIYA, T., 1951, *Prog. Theor. Phys.*, **6**, 342.
NÉEL, L., 1932 a, *Ann. Phys., Paris*, **17**, 5; 1932 b, *J. Phys. Radium*, **3**, 160; 1936 a, *Ann. Phys., Paris*, **5**, 232; 1936 b, *C. R. Acad. Sci., Paris*, **203**, 304; 1948, *Ann. Phys., Paris*, **3**, 137; 1949, *Ibid.*, **4**, 249.
NÉEL, L., and PAUTHENET, R., 1952, *C. R. Acad. Sci., Paris*, **234**, 1991.
PAUTHENET, R., and BOCHIROL, L., 1951, *J. Phys. Radium*, **12**, 249.
POULIS, N. J., 1952, *Commun. Phys. Lab. Univ. Leiden*, nos. 283 b, 287 a, 288 d.
POULIS, N. J., VAN DEN HAENDEL, J., UBBINK, J., POULIS, J. A., and GORTER, C. J., 1951, *Phys. Rev.*, **82**, 552.
SERRES, A., 1932, *Ann. Phys., Paris*, **17**, 53; 1947, *J. Phys. Radium*, **8**, 146.
SHULL, C. G., WOLLAN, E. O., and STRAUSER, W. A., 1951 a, *Phys. Rev.*, **81**, 483.
SHULL, C. G., STRAUSER, W. A., and WOLLAN, E. O., 1951 b, *Phys. Rev.*, **83**, 333.
SHULL, C. G., and WILKINSON, M. K., 1952, *Bull. Amer. Phys. Soc.*, **27**, 24.
STOUT, J. W., and GRIFFEL, M., 1949, *Phys. Rev.*, **76**, 144.
VERWEY, E. J., and DE BOER, J. H., 1936, *Rec. Trav. Chim., Pays-Bas*, **55**, 131.
VERWEY, E. J., and HEILMANN, E. L., 1947, *J. Chem. Phys.*, **15**, 174.
VAN VLECK, J. H., 1941, *J. Chem. Phys.*, **9**, 85.
WEISS, P., 1907, *J. Phys.*, **6**, 661.
YOSIDA, K., 1951, *Prog. Theor. Phys.*, **6**, 356; 1952, *Ibid.*, **7**, 25.
ZENER, C., 1952, *Phys. Rev.*, **85**, 324.

Spin Degeneracy and the Theory of Collective Electron Ferromagnetism

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ABSTRACT. The theory of ferromagnetism is often developed on the assumption that the exchange energy responsible for the magnetization is adequately represented as a sum of exchange integrals between pairs of electrons with mutually parallel spins. This is equivalent to using for the total wave function a determinant built up of one-electron functions. For the magnetized states of interest in ferromagnetism a single determinant wave function must be regarded as inadequate on account of the so-called spin or exchange degeneracy, which requires us to use instead appropriate linear combinations of the degenerate determinants. In the present paper a model is presented for which the results of neglecting or taking account of this spin degeneracy are identical. The model can be handled exactly and leads to equations for the free energy, magnetization, etc., which are a generalization of Stoner's theory of ferromagnetism to a system with two energy bands; these could be the overlapping 3d and 4s bands in the iron transition series. The calculations are not necessarily restricted to ferromagnetic metals and would apply equally well to those that are paramagnetic.

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§ 1. INTRODUCTION

It is possible to distinguish two main stages in the calculation of the quantum mechanical properties of the valence electrons in metals. In the first we calculate the energy of an electron moving in the ion-core field and in the average field of the remaining valence electrons; the energy of all the electrons together is then taken to be simply the sum of the resulting one-electron energies. This stage is represented by the elementary band theory of solids (Seitz 1940, especially Chapter 8). Thermal properties can be handled by using the simple Fermi–Dirac statistics. In the next stage we take the one-electron wave functions, which may be those found by some stage-one calculation, build up a product wave function Ψ with the correct symmetry properties and then calculate the energy of the selected configuration by using the true N-electron Hamiltonian. This more elaborate procedure is less often used in discussing electronic thermal properties, though one is forced in principle to use it in the theory of ferromagnetism. Generally the simple Fermi–Dirac statistics are not applicable in this approximation (Wohlfarth 1950).

Now in this second stage it is commonly assumed that the spin dependent energy of a state is a sum of exchange integrals for all those pairs of electrons with mutually parallel spin. This is equivalent to describing the whole system by a wave function which is a determinant of one-electron functions, each one-electron function being simply the product of an orbital space function and a spin function. The orbitals may be assumed localized about particular atoms as in the Heisenberg (1928) theory, or non-localized as, for example, in Slater's calculations (1936). In both cases the electronic interaction term $\Sigma_{i<j} e^2/r_{ij}$ in the Hamiltonian is treated as a perturbation, the eigenfunctions of the unperturbed Hamiltonian each being a determinant of one-electron functions. When however a given state (or configuration) contains only one electron in some orbitals, there will be a number of degenerate unperturbed determinant functions corresponding to the different ways of assigning spin functions (either α or β) to these singly occupied orbitals. This degeneracy is known as spin or exchange degeneracy. It follows that the correct wave function for calculating the perturbation energy due to the electron interactions is not a single determinant, as is frequently assumed in ferromagnetism, but some linear combination of the degenerate determinantal functions. The method of calculating the coefficients and the perturbation energy is familiar from the theory of atoms and molecules (see for example Slater 1929, or Condon and Shortley 1935) and leads to a classification of states by the eigenvalues of the square of the total spin vector operator and of the z component of the spin vector operator. Furthermore, Dirac (1929) showed that this problem was equivalent to a similar degeneracy problem, in which the perturbation part of the Hamiltonian was a sum of terms, each proportional to the scalar product of the spin vector operators of two electrons in singly occupied orbitals. This leads to a very convenient way of solving some exchange degeneracy problems, and one which we shall employ in the present paper. A very clear account of this method has recently been given by Corson (1951).

It is possible in principle to proceed from here to a calculation of magnetic and thermodynamic properties by constructing the partition function or sum-over-states, although for the large systems arising in the theory of ferromagnetism it is generally only possible to evaluate both the energy levels and the partition sum approximately. Bloch (1932) showed that to neglect spin degeneracy is justifiable at sufficiently high temperatures, where the partition function goes over into the function that would be obtained if we used single determinant wave functions rather than the correct linear combinations. Many accounts of the theory of ferromagnetism start either explicitly or implicitly from this high temperature approximation. It does not seem to have been noticed however that there is a model, probably nearly realized in practice, which can be handled exactly, and for which the results of including or neglecting the spin degeneracy are the same. We specify this model by the requirement that the available orbitals divide into two groups, A and B, such that the exchange integral between any two orbitals depends only on which group(s) they belong to. This includes the special case of a model with only one group or one common exchange integral. On this basis we shall derive exact equations for magnetization, free energy, etc., which prove to be a generalization of those used by Stoner (1938, 1939) in his theory of collective electron ferromagnetism. These equations are derived in the next section, and in the final § 3 we list several observations on them and on their relation to previous work in this field.

§ 2. EXPRESSION FOR THE FREE ENERGY

We suppose that the orbitals $\psi_j(\mathbf{r})$ of the 'ferromagnetic' electrons form a set of localized orthonormal functions extending throughout the magnetic 'domain', and that the inner shell electrons may be replaced by a suitable potential field. The sum of this field and that due to the nuclei we denote by $U(\mathbf{r})$. For definiteness the $\psi_j(\mathbf{r})$ may be supposed to be Bloch tight-binding wave functions (see Mott and Jones 1936), though in what follows we shall not need such an assumption explicitly. With each orbital ψ_j may be associated an energy ϵ_j, thus:

$$\epsilon_j = \int \psi_j^*(\mathbf{r}) \left\{ \frac{-\hbar^2}{2\boldsymbol{m}} \nabla^2 + U(\mathbf{r}) \right\} \psi_j(\mathbf{r})\, d\mathbf{r}. \qquad \ldots\ldots(2.1)$$

This may be regarded as the sum of the kinetic energy and the energy of interaction of the orbital ψ_j with the lattice. We also form the Coulomb and exchange integrals, denoted by J_{ij} and K_{ij} respectively in Slater's (1929) notation:

$$J_{ij} = \iint \psi_i^*(\mathbf{r}_1)\, \psi_i(\mathbf{r}_1) \frac{\mathbf{e}^2}{r_{12}} \psi_j^*(\mathbf{r}_2)\, \psi_j(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2, \qquad \ldots\ldots(2.2)$$

$$K_{ij} = \iint \psi_i^*(\mathbf{r}_1)\, \psi_i(\mathbf{r}_2) \frac{\mathbf{e}^2}{r_{12}} \psi_j(\mathbf{r}_1)\, \psi_j^*(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2. \qquad \ldots\ldots(2.3)$$

Dirac's result for the exchange problem may now be applied in the following form (Corson 1951, § 81); in solving the secular problem arising from the spin degeneracy the perturbation term in the Hamiltonian may be replaced by the following operator:

$$\mathbf{V} = \sum_{i<j} [J_{ij} - \tfrac{1}{2}(1 + 4\underline{\mathbf{s}}_i \cdot \underline{\mathbf{s}}_j) K_{ij}] + \sum_{j,\,\mu} (2J_{j\mu} - K_{j\mu}) + \sum_{\mu<\nu} (4J_{\mu\nu} - 2K_{\mu\nu}) + \sum_{\mu} J_{\mu\mu} - 2\beta H \sum_{i} \underline{\mathbf{s}}_{iz}, \qquad \ldots\ldots(2.4)$$

in which doubly-filled orbitals are denoted by a Greek letter and singly-filled orbitals by a Roman letter. $\underline{\mathbf{s}}_i$ is the spin vector operator for the electron in orbital i, and $\mathbf{s}_{iz}$ is the z component of this operator. The Bohr magneton has been denoted by β. The last term in eqn. (2.4), being the operator for the energy in the external magnetic field H, is not really part of the Dirac result, which concerns only the electronic interactions, but it may conveniently be added into the perturbation operator $\mathbf{V}$. The possible energies for the various spin states of a particular configuration are the eigenvalues of the matrix of $\mathbf{V}$.

We now apply this result to a model for which the whole set of available orbitals may be divided into two groups, A and B, such that all pairs of A orbitals have a common exchange integral K_A, all pairs of B orbitals have a common exchange integral K_B and all pairs formed from one A and one B orbital have a common exchange integral K_{AB}. The spin dependent part of $\mathbf{V}$ then becomes

$$\begin{aligned} & -2 \sum_{i<j} \underline{\mathbf{s}}_i . \underline{\mathbf{s}}_j K_{ij} \\ & = -2K_A \sum_{Ai<Aj} \underline{\mathbf{s}}_{Ai} \cdot \underline{\mathbf{s}}_{Aj} - 2K_B \sum_{Bi<Bj} \underline{\mathbf{s}}_{Bi} \cdot \underline{\mathbf{s}}_{Bj} - 2K_{AB} \sum_{Ai,\, Bj} \underline{\mathbf{s}}_{Ai} \cdot \underline{\mathbf{s}}_{Bj} \\ & = -2K_A \sum_{Ai<Aj} \underline{\mathbf{s}}_{Ai} \cdot \underline{\mathbf{s}}_{Aj} - 2K_B \sum_{Bi<Bj} \underline{\mathbf{s}}_{Bi} \cdot \underline{\mathbf{s}}_{Bj} - 2K_{AB} \underline{\mathbf{S}}_A \cdot \underline{\mathbf{S}}_B \\ & = -K_A\Big(\underline{\mathbf{S}}_A^2 - \sum_{Ai} \underline{\mathbf{s}}_{Ai}^2\Big) - K_B\Big(\underline{\mathbf{S}}_B^2 - \sum_{Bi} \underline{\mathbf{s}}_{Bi}^2\Big) - 2K_{AB} \underline{\mathbf{S}}_A \cdot \underline{\mathbf{S}}_B\,, \qquad \ldots\ldots(2.5) \end{aligned}$$

where

$$\underline{\mathbf{S}}_A = \sum_{Ai} \underline{\mathbf{s}}_{Ai} \quad \text{and} \quad \underline{\mathbf{S}}_B = \sum_{Bi} \underline{\mathbf{s}}_{Bi} \qquad \ldots\ldots(2.6)$$

are the total spin vector operators for those electrons in A and B orbitals respectively. Thus $\underline{\mathbf{S}}_A^2$ and $\underline{\mathbf{S}}_B^2$ commute with the right-hand side of eqn. (2.5) and, of course, with $\underline{\mathbf{S}}_{Az} + \underline{\mathbf{S}}_{Bz} = \underline{\mathbf{S}}_z$ and $\underline{\mathbf{S}}^2 = (\underline{\mathbf{S}}_A + \underline{\mathbf{S}}_B)^2$; therefore, since the unperturbed Hamiltonian is spin-independent, $\underline{\mathbf{S}}_A^2$ and $\underline{\mathbf{S}}_B^2$, as well as $\underline{\mathbf{S}}^2$ and $\underline{\mathbf{S}}_z$, are constants of the motion with eigenvalues $S_A(S_A+1)$ and $S_B(S_B+1)$ respectively. For a configuration with n A orbitals and m B orbitals singly occupied (n and m are assumed even for convenience) the numbers S_A and S_B may be any of the integers from 0 to $n/2$ and 0 to $m/2$ respectively. The eigenvalues of $\underline{\mathbf{S}}^2$ are $S(S+1)$ with the allowed values of S being the integers from $S_A + S_B$ to $|S_A - S_B|$, in the usual way for the sum of two angular momentum vectors (Corson 1951, § 21). Lastly, the eigenvalues of $\mathbf{S}_z$ are $S, S-1, \ldots -S+1, -S$. Since $2\underline{\mathbf{S}}_A . \underline{\mathbf{S}}_B = \underline{\mathbf{S}}^2 - \underline{\mathbf{S}}_A^2 - \underline{\mathbf{S}}_B^2$, we see that the secular matrix of $\mathbf{V}$ has eigenvalues

$$\begin{aligned} V = & \sum_{i<j} J_{ij} + \sum_{j,\mu} 2J_{j\mu} + \sum_{\mu<\nu} 4J_{\mu\nu} + \sum_{\mu} J_{\mu\mu} - \frac{K_A N_A^2}{4} - \frac{K_B N_B^2}{4} - \frac{K_{AB} N_A N_B}{2} \\ & + S_B^2(K_{AB} - K_B) + S_A^2(K_{AB} - K_A) - S^2 K_{AB} - 2\beta H S_z \\ = & V_0 - 2\beta H S_z, \qquad \ldots\ldots(2.7) \end{aligned}$$

where N_A and N_B are the total numbers of electrons in A and B orbitals, respectively. Since N_A, N_B, S_A, S_B and S are all very large, of the order of the number of atoms in a magnetic domain, the distinction between $S(S+1)$ and S^2, $N_A(N_A-1)$ and N_A^2, etc., has been ignored in obtaining eqn. (2.7). For a given configuration which we denote by $C(n, N_A\,;\ m, N_B)$, the number of (spin) states with given values of S_A, S_B, S and S_z is obtained by a simple generalization of the *Branching Rule* (Corson 1951, § 82). This number, which we shall denote by $g(n, S_A : m, S_B)$, is

$$g(n, S_A\,;\ m, S_B) = \left[\binom{n}{\tfrac{1}{2}n + S_A} - \binom{n}{\tfrac{1}{2}n + S_A + 1}\right]\left[\binom{m}{\tfrac{1}{2}m + S_B} - \binom{m}{\tfrac{1}{2}m + S_B + 1}\right]. \qquad \ldots\ldots(2.8)$$

The total energy E of each of the states of given S_A, S_B, S and S_z is obtained by adding to V the sum of the orbital energies for the configuration $C(n, N_A\,;\ m, N_B)$. This can be written as

$$\sum_{Ar} u_{Ar} \epsilon_{Ar} + \sum_{Br} u_{Br} \epsilon_{Br}, \qquad \ldots\ldots(2.9)$$

where the occupation numbers $u_{\mathrm{A}r}$ and $u_{\mathrm{B}r}$ are 0, 1, 2, according as the orbitals Ar and Br are unoccupied, singly or doubly occupied. (In eqn. (2.9) and the following we use a Roman letter to denote any orbital, not necessarily one singly occupied as formerly.) In this notation to specify $C(n, N_{\mathrm{A}}; m, N_{\mathrm{B}})$ is to specify the two sets of numbers $(u_{\mathrm{A}r})$ and $(u_{\mathrm{B}r})$. Obviously

$$\sum_{\mathrm{A}r} u_{\mathrm{A}r} = N_{\mathrm{A}} \quad \text{and} \quad \sum_{\mathrm{B}r} u_{\mathrm{B}r} = N_{\mathrm{B}} \qquad \ldots\ldots(2.10)$$

for all sets $(u_{\mathrm{A}r})$ and $(u_{\mathrm{B}r})$.

This completes the enumeration of the states and corresponding energies. To derive now the thermodynamic properties of the system the most direct way is to evaluate the partition function Q, i.e. we must sum $g(n, S_{\mathrm{A}}; m, S_{\mathrm{B}})\,\mathrm{e}^{-E/kT}$ over all spin states, over all configurations and over all allowed distributions of the N electrons between the two groups. Thus

$$Q = \sum_{N_{\mathrm{A}}=0}^{N} \sum_{N_{\mathrm{B}}=0}^{N-N_{\mathrm{A}}} \sum_{S_{\mathrm{B}}=0}^{N_{\mathrm{B}}/2} \sum_{S_{\mathrm{A}}=0}^{N_{\mathrm{A}}/2} \sum_{S=|S_{\mathrm{A}}-S_{\mathrm{B}}|}^{S_{\mathrm{A}}+S_{\mathrm{B}}} \sum_{S_z=0}^{S} \sum_{m=2S_{\mathrm{B}}}^{N_{\mathrm{B}}} \sum_{n=2S_{\mathrm{A}}}^{N_{\mathrm{A}}} \sum_{C(n, N_{\mathrm{A}};\, m, N_{\mathrm{B}})} \times g(n, S_{\mathrm{A}}; m, S_{\mathrm{B}})\,\mathrm{e}^{-E/kT}. \qquad \ldots\ldots(2.11)$$

As all the thermodynamic quantities depend directly not on Q but on $\ln Q$, it is justifiable to replace Q by

$$Q' = \sum_{m=2S_{\mathrm{B}}}^{N_{\mathrm{B}}} \sum_{n=2S_{\mathrm{A}}}^{N_{\mathrm{A}}} \sum_{C(n, N_{\mathrm{A}};\, m, N_{\mathrm{B}})} g(n, S_{\mathrm{A}}; m, S_{\mathrm{B}})\,\mathrm{e}^{-E/kT}, \qquad \ldots\ldots(2.12)$$

together with the conditions that this Q' be made a maximum with respect to S_z, S, S_{A}, S_{B} and N_{A}. The five equations which result give the (thermodynamically) mean values of these quantities. We denote such mean values by a bar. Substituting for E we find that

$$\overline{S}_z = \overline{S} = \overline{S}_{\mathrm{A}} + \overline{S}_{\mathrm{B}}. \qquad \ldots\ldots(2.13)$$

In the following we replace S_z and S in Q' by $S_{\mathrm{A}} + S_{\mathrm{B}}$, maximizing the resulting expression with respect to S_{A} and S_{B}. This is legitimate since there are no cross terms such as SS_{A} or S_zS_{A}. The remaining problem, the evaluation of Q', is now possible accurately only if we make additional assumptions about the coulomb integrals J_{ij}, which so far we have left entirely arbitrary. Such restrictions on the J_{ij} are not necessary for the equivalence of the two free energies calculated neglecting and also including spin degeneracy; this always holds under the conditions we have imposed on the exchange integrals K_{ij}. But to complete the calculation accurately we assume there to be only three distinct coulomb integrals J_{A}, J_{B} and J_{AB} analogous to the three exchange integrals K_{A}, K_{B} and K_{AB}. There seems in fact little point in working with a more general set of coulomb integrals unless we also take a general set of exchange integrals. The function Q' becomes

$$Q' = \exp \frac{1}{kT}(2\beta H(S_{\mathrm{A}} + S_{\mathrm{B}}) - V_0)$$
$$\times \sum_{n=2S_{\mathrm{A}}}^{N_{\mathrm{A}}} \sum_{m=2S_{\mathrm{B}}}^{N_{\mathrm{B}}} \sum_{C(n, N_{\mathrm{A}};\, m, N_{\mathrm{B}})} g(n, S_{\mathrm{A}}; n, S_{\mathrm{B}}) \exp - \frac{1}{kT}\left(\sum_{\mathrm{A}r} u_{\mathrm{A}r}\epsilon_{\mathrm{A}r} + \sum_{\mathrm{B}r} u_{\mathrm{B}r}\epsilon_{\mathrm{B}r}\right), \qquad \ldots\ldots(2.14)$$

where

$$V_0 = \tfrac{1}{4}N_{\mathrm{A}}^2(2J_{\mathrm{A}} - K_{\mathrm{A}}) + \tfrac{1}{4}N_{\mathrm{B}}^2(2J_{\mathrm{B}} - K_{\mathrm{B}}) + \tfrac{1}{2}N_{\mathrm{A}}N_{\mathrm{B}}(2J_{\mathrm{AB}} - K_{\mathrm{AB}}) - K_{\mathrm{A}}S_{\mathrm{A}}^2 - K_{\mathrm{B}}S_{\mathrm{B}}^2 - 2K_{\mathrm{AB}}S_{\mathrm{A}}S_{\mathrm{B}} \qquad \ldots\ldots(2.15)$$

is independent of the configuration of the system so long as N_{A} electrons are in A orbitals and N_{B} in B orbitals.

Consider the contribution to Q' from the term $\binom{n}{\frac{1}{2}n+S_{\rm A}}\binom{m}{\frac{1}{2}m+S_{\rm B}}$ in $g(n, S_{\rm A};\ m, S_{\rm B})$. The first factor is the number of ways in which $\frac{1}{2}n+S_{\rm A}$ upward spins and $\frac{1}{2}n-S_{\rm A}$ downward spins can be distributed over the n singly occupied A orbitals. Similarly the second factor is the number of ways $\frac{1}{2}m+S_{\rm B}$ upward spins and $\frac{1}{2}m-S_{\rm B}$ downward spins can be distributed over the singly occupied B orbitals. For all these arrangements $\Sigma_{{\rm A}r}u_{{\rm A}r}\epsilon_{{\rm A}r}+\Sigma_{{\rm B}r}u_{{\rm B}r}\epsilon_{{\rm B}r}$ has the same value. We see therefore that

$$\sum_{n=2S_{\rm A}}^{N_{\rm A}}\sum_{m=2S_{\rm B}}^{N_{\rm B}}\sum_{C(n,\,N_{\rm A};\ m,\,N_{\rm B})}\binom{n}{\frac{1}{2}n+S_{\rm A}}\binom{m}{\frac{1}{2}m+S_{\rm B}}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm A}r}u_{{\rm A}r}\epsilon_{{\rm A}r}+\sum_{{\rm B}r}u_{{\rm B}r}\epsilon_{{\rm B}r}\right)\right\}$$
$$=\left[\sum_{n=2S_{\rm A}}^{N_{\rm A}}\sum_{C_{\rm A}(n,\,N_{\rm A})}\binom{n}{\frac{1}{2}n+S_{\rm A}}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm A}r}u_{{\rm A}r}\epsilon_{{\rm A}r}\right)\right\}\right]$$
$$\times\left[\sum_{m=2S_{\rm B}}^{N_{\rm B}}\sum_{C_{\rm B}(m,\,N_{\rm B})}\binom{m}{\frac{1}{2}m+S_{\rm B}}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm B}r}u_{{\rm B}r}\epsilon_{{\rm B}r}\right)\right\}\right],$$

may be rewritten as

$$\left[\sum_{(p_{{\rm A}r})}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm A}r}p_{{\rm A}r}\epsilon_{{\rm A}r}\right)\right\}\right]\left[\sum_{(q_{{\rm A}r})}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm A}r}q_{{\rm A}r}\epsilon_{{\rm A}r}\right)\right\}\right]$$
$$\times\left[\sum_{(p_{{\rm B}r})}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm B}r}p_{{\rm B}r}\epsilon_{{\rm B}r}\right)\right\}\right]\left[\sum_{(q_{{\rm B}r})}\exp\left\{-\frac{1}{\boldsymbol{k}T}\left(\sum_{{\rm B}r}q_{{\rm B}r}\epsilon_{{\rm B}r}\right)\right\}\right], \qquad ..(2.16)$$

where the new occupation numbers $p_{{\rm A}r}, q_{{\rm A}r}, p_{{\rm B}r}$ and $q_{{\rm B}r}$ are either 0 or 1. The p's may be regarded as occupation numbers for parallel spins and the q's for anti-parallel spins. The outer summations in the four factors of eqn. (2.16) are over all sets of occupation numbers satisfying

$$\sum_{{\rm A}r}p_{{\rm A}r}=\tfrac{1}{2}N_{\rm A}+S_{\rm A},\quad \sum_{{\rm A}r}q_{{\rm A}r}=\tfrac{1}{2}N_{\rm A}-S_{\rm A},$$
$$\sum_{{\rm B}r}p_{{\rm B}r}=\tfrac{1}{2}N_{\rm B}+S_{\rm B},\quad \sum_{{\rm B}r}q_{{\rm B}r}=\tfrac{1}{2}N_{\rm B}-S_{\rm B}.$$

Each factor in (2.16) is in fact a simple Fermi–Dirac partition function ; if we denote these by $Z_{\rm A}(\nu)$ and $Z_{\rm B}(\nu)$ for ν particles distributed over the A orbitals only and B orbitals only, then (2.16) is just

$$+Z_{\rm A}(\tfrac{1}{2}N_{\rm A}+S_{\rm A})Z_{\rm A}(\tfrac{1}{2}N_{\rm A}-S_{\rm A})Z_{\rm B}(\tfrac{1}{2}N_{\rm B}+S_{\rm B})Z_{\rm B}(\tfrac{1}{2}N_{\rm B}-S_{\rm B}).$$

Dealing with the contributions to Q' of the other three terms in $g(n, S_{\rm A};\ m, S_{\rm B})$ in the same way we get

$$-Z_{\rm A}(\tfrac{1}{2}N_{\rm A}+S_{\rm A})Z_{\rm A}(\tfrac{1}{2}N_{\rm A}-S_{\rm A})Z_{\rm B}(\tfrac{1}{2}N_{\rm B}+S_{\rm B}+1)Z_{\rm B}(\tfrac{1}{2}N_{\rm B}-S_{\rm B}-1)$$
$$-Z_{\rm A}(\tfrac{1}{2}N_{\rm A}+S_{\rm A}+1)Z_{\rm A}(\tfrac{1}{2}N_{\rm A}-S_{\rm A}-1)Z_{\rm B}(\tfrac{1}{2}N_{\rm B}+S_{\rm B})Z_{\rm B}(\tfrac{1}{2}N_{\rm B}-S_{\rm B})$$
$$+Z_{\rm A}(\tfrac{1}{2}N_{\rm A}+S_{\rm A}+1)Z_{\rm A}(\tfrac{1}{2}N_{\rm A}-S_{\rm A}-1)Z_{\rm B}(\tfrac{1}{2}N_{\rm B}+S_{\rm B}+1)Z_{\rm B}(\tfrac{1}{2}N_{\rm B}-S_{\rm B}-1).$$

The sum of these four terms can be simplified by using the relation

$$\frac{Z(\nu)}{Z(\nu+1)}=\lambda(\nu), \qquad ......(2.17)$$

where λ, the usual parameter arising in the Fermi–Dirac problem, is determined by the number of particles ν:

$$\nu=\Sigma\,[\lambda^{-1}\exp(\epsilon_r/\boldsymbol{k}T)+1]^{-1} \qquad ......(2.18)$$

In this way we find that

$$\begin{aligned}\ln Q' = {} & 2(S_A+S_B)\frac{\beta H}{\boldsymbol{k}T}-\frac{V_0}{\boldsymbol{k}T} \\ & +\ln\{Z_A(\tfrac{1}{2}N_A+S_A)\,Z_A(\tfrac{1}{2}N_A-S_A)\,Z_B(\tfrac{1}{2}N_B+S_B)\,Z_B(\tfrac{1}{2}N_B-S_B)\} \\ & +\ln\left\{1-\frac{\lambda_B(\tfrac{1}{2}N_B-S_B)}{\lambda_B(\tfrac{1}{2}N_B+S_B)}\right\}\left\{1-\frac{\lambda_A(\tfrac{1}{2}N_A-S_A)}{\lambda_A(\tfrac{1}{2}N_A+S_A)}\right\}. \qquad \ldots\ldots(2.19)\end{aligned}$$

The last term is entirely negligible except when S_A and S_B tend to zero, as at the Curie point. Even then, however, it is only of the order of $\ln N$ and so may be neglected since $\ln Q$ must be proportional to N. The remainder of eqn. (2.19) is just the partition function we would obtain if we neglected spin degeneracy; $2S_A$ would then be the difference between the numbers of parallel and antiparallel spins in A orbitals, with a similar interpretation for $2S_B$.

It only remains to substitute for Z_A and Z_B to obtain an expression for the free energy F. This may be simplified by using the condition that F be a minimum with respect to S_A and S_B. We also replace the discrete sums over orbitals by integrals by introducing density of states (orbitals) factors $n_A(\epsilon)$ and $n_B(\epsilon)$. Then

$$\begin{aligned}F = {} & \overline{N}_A\eta_A+\overline{N}_B\eta_B+\tfrac{1}{4}\overline{N}_A{}^2(2J_A-K_A)+\tfrac{1}{4}\overline{N}_B{}^2(2J_B-K_B) \\ & +\tfrac{1}{2}\overline{N}_A\overline{N}_B(2J_{AB}-K_{AB})-\overline{S}_A{}^2K_A-\overline{S}_B{}^2K_B-2\overline{S}_A\overline{S}_BK_{AB} \\ & +\int_A n_A(\epsilon)\ln\left\{1+\exp\frac{1}{\boldsymbol{k}T}(\eta_A-\epsilon+K_A\overline{S}_A+K_{AB}\overline{S}_B+\beta H)\right\}d\epsilon \\ & +\int_A n_A(\epsilon)\ln\left\{1+\exp\frac{1}{\boldsymbol{k}T}(\eta_A-\epsilon-K_A\overline{S}_A-K_{AB}\overline{S}_B-\beta H)\right\}d\epsilon \\ & +\int_B n_B(\epsilon)\ln\left\{1+\exp\frac{1}{\boldsymbol{k}T}(\eta_B-\epsilon+K_B\overline{S}_B+K_{AB}\overline{S}_A+\beta H)\right\}d\epsilon \\ & +\int_B n_B(\epsilon)\ln\left\{1+\exp\frac{1}{\boldsymbol{k}T}(\eta_B-\epsilon-K_B\overline{S}_B-K_{AB}\overline{S}_A-\beta H)\right\}d\epsilon, \\ & \qquad \ldots\ldots(2.20)\end{aligned}$$

with the following five equations connecting η_A, η_B, $\overline{S}_A$, $\overline{S}_B$, $\overline{N}_A$ and $\overline{N}_B$.

$$\eta_A-\eta_B=\tfrac{1}{2}(2J_B-K_B)\overline{N}_B-\tfrac{1}{2}(2J_A-K_A)\overline{N}_A+\tfrac{1}{2}(2J_{AB}-K_{AB})(\overline{N}_A-\overline{N}_B), \qquad \ldots\ldots(2.21)$$

$$\tfrac{1}{2}\overline{N}_A\pm\overline{S}_A=\int_A n_A(\epsilon)\left[\exp\frac{1}{\boldsymbol{k}T}(\epsilon-\eta_A\mp K_A\overline{S}_A\mp K_{AB}\overline{S}_B\mp\beta H)+1\right]^{-1}d\epsilon \qquad \ldots\ldots(2.22)$$

$$\tfrac{1}{2}\overline{N}_B\pm\overline{S}_B=\int_B n_B(\epsilon)\left[\exp\frac{1}{\boldsymbol{k}T}(\epsilon-\eta_B\mp K_B\overline{S}_B\mp K_{AB}\overline{S}_A\mp\beta H)+1\right]^{-1}d\epsilon. \qquad \ldots\ldots(2.23)$$

These equations can be applied to a system with two energy bands which may or may not overlap one another for a certain range of ϵ; they can be worked out fully for simple forms of $n_A(\epsilon)$ and $n_B(\epsilon)$ by using the numerical tables of McDougall and Stoner (1938) and of Rhodes (1950). We shall not attempt here the detailed application of these equations, but append several general comments prompted by the above calculation.

§ 3. GENERAL REMARKS

(i) *On the Density of States Functions*

The functions $n_{\mathrm{A}}(\epsilon)$ and $n_{\mathrm{B}}(\epsilon)$ which we have introduced are not identical with the density of states functions usually constructed by energy band calculations. The energy ϵ above is the sum of kinetic energy and energy of interaction of the orbital function $\psi(\mathbf{r})$ with the lattice; the energies obtained in a band calculation (for example by the cellular method) are approximations to the energy parameters in the Hartree–Fock equations, and these, as is well known, include a contribution from electronic coulomb and exchange interactions. This is probably no practical disadvantage since, as already mentioned, eqns. (2.20) etc. can only be worked out for certain assumed forms of $n_{\mathrm{A}}(\epsilon)$ and $n_{\mathrm{B}}(\epsilon)$, and it seems likely that we can obtain in this way an equally good representation of the density of states in our energy ϵ as of the density of states in the ϵ of the energy band calculations.

(ii) *Application to Iron, Cobalt and Nickel*

The A and B groups may be tentatively identified with the 3d and 4s bands in iron, cobalt and nickel, where it is generally assumed some of the 4s orbitals have energies ϵ in common with some of the 3d orbitals. (Equations (2.20) to (2.23) do not necessarily lead to ferromagnetism, however, and we could equally well identify A and B with the 4d and 5s bands of the paramagnetics platinum and palladium.) If we can neglect the B orbitals as of lesser importance than the A, then the equations for the magnetization are an obvious generalization of those used by Stoner (1938, eqns. (2.10), (2.11)). If M be the magnetic moment then

$$\frac{M}{\beta}=2\overline{S}_{\mathrm{A}}=\int_{\mathrm{A}} n_{\mathrm{A}}(\epsilon)\left[\exp\frac{1}{\boldsymbol{k}T}(\epsilon-\eta_{\mathrm{A}}-K_{\mathrm{A}}\overline{S}_{\mathrm{A}}-\beta H)+1\right]^{-1}d\epsilon$$
$$-\int_{\mathrm{A}} n_{\mathrm{A}}(\epsilon)\left[\exp\frac{1}{\boldsymbol{k}T}(\epsilon-\eta_{\mathrm{A}}+K_{\mathrm{A}}\overline{S}_{\mathrm{A}}+\beta H)+1\right]^{-1}d\epsilon, \quad \ldots\ldots(3.1)$$

with

$$N=\int_{\mathrm{A}} n_{\mathrm{A}}(\epsilon)\left[\exp\frac{1}{\boldsymbol{k}T}(\epsilon-\eta_{\mathrm{A}}-K_{\mathrm{A}}\overline{S}_{\mathrm{A}}-\beta H)+1\right]^{-1}d\epsilon$$
$$+\int_{\mathrm{A}} n_{\mathrm{A}}(\epsilon)\left[\exp\frac{1}{\boldsymbol{k}T}(\epsilon-\eta_{\mathrm{A}}+K_{\mathrm{A}}\overline{S}_{\mathrm{A}}+\beta H)+1\right]^{-1}d\epsilon. \quad \ldots\ldots(3.2)$$

These equations have been worked out by Stoner for $n_{\mathrm{A}}(\epsilon)$ proportional to $\epsilon^{1/2}$ and by Wohlfarth (1951) for $n_{\mathrm{A}}(\epsilon)$ independent of ϵ. In both cases $N_{\mathrm{A}}K_{\mathrm{A}}/2$ is to be identified with their parameter $\boldsymbol{k}\theta'$; no other interpretation of $\boldsymbol{k}\theta'$ has so far been proposed.

Equations (3.1) and (3.2) for a system with only one distinct exchange integral K and one coulomb integral J should also have been obtained by Hirone (1938), for this was precisely the model he assumed. In his calculations of the partition function, however, Hirone omitted the sum over all configurations of a given number of singly occupied levels, and thus obtained an incorrect result.*

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* Dr. H. Watanabe in a recent private communication to the author has said that Hirone and Miyahara subsequently corrected this error in a paper entitled "Ferromagnetism in Semi-Conductors" which appeared in *Nippon Sugaku-Butsuri Gakkai-shi* (1943), **7**, 92. Since this paper is in Japanese and not generally accessible in the West we have considered it worth while to refer here to Hirone's earlier omission.

(iii) *More General Models*

The particular model that we have examined is the most general for which the calculated properties are the same whether we include or neglect spin degeneracy. Neglecting spin degeneracy we would say that the energy is entirely determined by the two quantum numbers $(S_z)_A$ and $(S_z)_B$; including spin degeneracy the energy is specified by the two total spin quantum numbers S_A and S_B. However, for a more complicated model, for example one with three groups of orbitals, this is no longer true. Neglecting spin degeneracy, the energy would be completely determined by $(S_z)_A$, $(S_z)_B$, $(S_z)_C$ etc., although including spin degeneracy the energy is not now determined uniquely by S_A, S_B, S_C etc.

For these more general systems the equivalence of the results obtained by neglecting and including spin degeneracy is restored only if we make the mean value approximation familiar in the simple Heisenberg theory. (We note that such an approximation in a general model with non-localized orbitals does not lead directly to Stoner's theory in the way that it should do if this were a 'zeroth-order approximation' as has been suggested by Van Vleck (1945).) In developing more accurate theories it seems likely that the correct expressions for the eigen-energies are required. This will apply not only in the theory of ferromagnetism; taking account of the spin degeneracy will modify the results whenever the average number of singly occupied levels $\bar{n}$ is different from zero, and for this it is *not* necessary that $\bar{S}$ be different from zero; i.e. the equilibrium spin state *could* be a singlet. For example, in the calculation of the influence of the exchange energy on the specific heat of free electrons (Wohlfarth 1950, Lidiard 1951) $\bar{n}$ is not zero, although so far no account has been taken of spin degeneracy. It is possible that inclusion of spin degeneracy would remove some of the notable disagreement between this calculation and experiment. Work to examine this possibility is in progress.

REFERENCES

BLOCH, F., 1932, *Z. Phys.*, **74**, 295.
CONDON, E. U., and SHORTLEY, G. H., 1935, *The Theory of Atomic Spectra* (Cambridge : University Press).
CORSON, E. M., 1951, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (London : Blackie).
DIRAC, P. A. M., 1929, *Proc. Roy. Soc.* A, **123**, 714.
HEISENBERG, W., 1928, *Z. Phys.*, **49**, 619.
HIRONE, T., 1938, *Sci. Rep. Tôhoku Imp. Univ.*, **27**, 101.
LIDIARD, A. B., 1951, *Phil. Mag.*, **42**, 1325.
MCDOUGALL, J., and STONER, E. C., 1938, *Phil. Trans. Roy. Soc.* A, **237**, 67.
MOTT, N. F., and JONES, H., 1936, *The Theory of the Properties of Metals and Alloys* (Oxford : University Press).
RHODES, P., 1950, *Proc. Roy. Soc.* A, **204**, 396.
SEITZ, F., 1940, *Modern Theory of Solids* (New York : McGraw–Hill).
SLATER, J. C., 1929, *Phys. Rev.*, **34**, 1293; 1936, *Ibid.*, **49**, 537 and 931.
STONER, E. C., 1938, *Proc. Roy. Soc.* A, **165**, 372; 1939, *Ibid.*, **169**, 339.
VAN VLECK, J. H., 1945, *Rev. Mod. Phys.*, **17**, 27.
WOHLFARTH, E. P., 1950, *Phil. Mag.*, **41**, 534; 1951, *Ibid.*, **42**, 374.

Proton Magnetic Resonance and Molecular Motion in Solids

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ABSTRACT. Proton magnetic resonance widths and relaxation times have been measured in ammonium chloride, bromide and iodide, methyl alcohol and dimethyl sulphate from 90° K to 290° K. Line width transitions were observed in NH_4Cl and NH_4Br at 135° K and 99° K respectively. There were no sharp changes in either the relaxation time or line width at the temperatures of the λ-specific heat anomalies of the ammonium salts. Evidently, there is no marked increase in the rate of rotation of the ammonium ion at these transitions. The results for NH_4Br suggest that rotation of the NH_4^+ ion is hindered by a potential barrier of about 3 500 cal/mole. The N–H distance is $1{\cdot}03 \pm 0{\cdot}01$ Å. The line width and relaxation time show pronounced changes at the λ-point of methyl alcohol, indicating a sudden change in the motion of the CH_3OH molecule. In solid dimethyl sulphate, a narrow line of small amplitude appears at about 170° K.

§ 1. INTRODUCTION: NUCLEAR RESONANCE AND MOLECULAR MOTION

An atomic nucleus of spin s and magnetic moment μ in a magnetic field H possesses $(2s+1)$ energy states separated by energy differences $\mu H/s$. In molecular beam experiments, Rabi, Zacharias, Millman and Kusch (1938) demonstrated that transitions between adjacent states may be induced by an oscillatory magnetic field perpendicular to the main field H and having a frequency ν given by $\boldsymbol{h}\nu = \mu H/s$ or $2\pi\nu = \gamma H$ where $\gamma = \mu/(s\boldsymbol{h}/2\pi)$ the gyromagnetic ratio for the nucleus.

When Purcell, Torrey and Pound (1946) and Bloch, Hansen and Packard (1946) succeeded in detecting these transitions in bulk matter electromagnetically, it was found that while the resonance field H for a given frequency is determined by the gyromagnetic ratio of the particular nucleus investigated, the shape and intensity of the resonance line are determined by the molecular conditions in the substance chosen. Since each nucleus is subject to a magnetic field due to its neighbours, resonance at a given frequency is observed as a more or less broad line spread over a range of magnetic fields corresponding to the distribution of the internal fields. In diamagnetic solids the only important contribution to the nuclear magnetic resonance line width comes from magnetic interaction between neighbouring nuclei. When the nuclei are stationary a formula for the second moment or mean square width of the line has been given by Van Vleck (1948). Gutowsky, Kistiakowsky, Pake and Purcell (1949) have shown that in many cases widths and shapes of nuclear resonance lines may be used to deduce internuclear distances in the solid state.

Molecular motion causes the internuclear fields to fluctuate, and if many fluctuations occur during the lifetime of the spin states, it is the average value of the internal fields that determines the line width. As these lifetimes are often greater than 10^{-5} second, even comparatively slow molecular motion may

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considerably reduce the line widths (Bloembergen, Purcell and Pound 1948). Bitter suggested that observations on the line width of nuclear resonance in solids would give information on molecular motion (Bitter, Alpert, Poss, Lehr and Lin 1947). In particular, it was thought that definite information could be obtained with regard to certain λ-anomalies in the variation of the specific heat with temperature in substances such as methane, methyl alcohol, the hydrogen halides and ammonium salts. If the λ-point marked the onset of molecular rotation (Pauling 1930) we should expect a very marked narrowing of the proton magnetic resonance as the temperature is raised through the λ-point. If on the other hand, it is due to an order–disorder transition (Frenkel 1935) the magnetic resonance would be little affected.

In the absence of electronic paramagnetism, the internal fields acting on a given nucleus may be classified under two heads:

(*a*) The field due to the magnetic moments of nuclei in the same molecule as the nucleus considered, and sometimes to the molecular magnetic moment of this molecule; this field is generally the major part of the internal field, since the separation of nuclei in the same molecule is less than that of nuclei in adjacent molecules. If molecular rotation, either free or hindered, or rotational oscillation causes this field to fluctuate sufficiently rapidly, it is the average value over the motion which is effective. Often, as in the ammonium halides, this average is zero.

(*b*) The field due to the magnetic moments of nuclei in neighbouring molecules, and sometimes to their molecular magnetic moments. When relative motion of molecules occurs, this field fluctuates with a period of the order of the time for the radius vector joining two molecules to turn through a large angle, say 90°. In all liquids with normal viscosities, molecular translational motion is sufficiently rapid for this class of internal field to average to zero as far as radio-frequency resonance is concerned. In solids molecular rotation will reduce this field by an amount dependent on the ratio of the intermolecular distance to the radius of rotation. It is calculated that in ammonium bromide, considered below, in which the separation of adjacent ions is 4·0 Å, rotation of the protons of the NH_4 ion about the nitrogen with a radius of 1·0 Å will reduce this intermolecular field from an r.m.s. value of 2·3 gauss to 1·9 gauss. Andrew (1950) has calculated that in the normal paraffins molecular rotation will reduce the r.m.s. intermolecular field from 2·8 gauss to 1·6 gauss. These calculations are in good agreement with experiment, and may be taken as typical. In some solids, however, the nuclear resonance lines are narrower than the limit of measurement set by inhomogeneities of the applied field (say 0·1 gauss). This is not compatible with the supposition that the only molecular motion is independent rotational motion about fixed centres. Gutowsky (1951) and Norberg and Schlichter (1951) have shown that self-diffusion accounts satisfactorily for the very narrow nuclear resonance lines observed in sodium metal. As the temperature is raised the diffusion frequency increases until it produces fluctuations of the internuclear fields during the lifetime of the spin states, reducing the effective interaction field to zero. It may be necessary to consider such a molecular motion in the other cases in which very narrow lines are observed in solids.

A second way in which molecular motion affects nuclear resonance is through the spin–lattice relaxation time. The nuclear magnetic moment of the specimen in a given magnetic field is inversely proportional to the temperature of the nuclear spin system (Curie's law of paramagnetism). Application of an oscillatory field near the resonance frequency results in the absorption of energy from the field into the spin system. If this energy cannot be transferred sufficiently rapidly from the spin system to the molecular lattice, the temperature of the spin system will rise and the nuclear magnetization will be reduced. This effect shows itself as a saturation of the absorption in high intensities of oscillatory field. From measurements of this saturation effect the time constant for the transfer of energy between the spins and the lattice—the spin–lattice relaxation time—can be determined. When molecular motion takes place the important mechanism for the transfer of energy from the spins to the lattice is by means of transitions induced by components of the fluctuating internuclear fields at frequencies near the resonance value. Bloembergen, Purcell and Pound (1948) have given a theory relating the relaxation times in liquids to the Debye time constant for molecular motion and hence to the viscosity of the liquid. In solids in which molecular motion occurs, a somewhat similar relation can be expected to hold between the spin–lattice relaxation time and the period of molecular motion. In the experiments below an ammonium bromide, relaxation time measurements have been applied to the estimation of the frequency of molecular rotation at temperatures between 90° K and 290° K.

§ 2. APPARATUS

Except for one or two experiments, all measurements have been made at a frequency of 8·155 Mc/s provided by a crystal-controlled oscillator. For protons $\gamma = 2{\cdot}675 \times 10^4$ gauss^{-1} sec^{-1}, giving a resonance field of 1 915 gauss. The radio-frequency circuit used resembles that of Bloch, Hansen and Packard (1946) in that resonance is observed by the voltage induced in a secondary coil surrounding the specimen instead of by the change in voltage across the primary coil providing the oscillatory field. By disposing the two coils at right angles the coupling between them may be made so small that no special balancing circuits are necessary to prevent saturation of the detecting system by direct pick-up from the oscillator. To distinguish the resonance signal from the background, an a.c. modulation method is used (Bloembergen, Purcell and Pound 1948). An audio-frequency field whose amplitude H_s is a small fraction of the width of the resonance line is superimposed on the main steady field H by means of auxiliary sweep coils round the magnet pole-pieces. In a region where the resonance response varies with the magnetic field, for example on the flanks of a resonance absorption curve, this small variation of magnetic field causes the output of the detector to vary in the same way. This variation of detector output is amplified by a tuned audio-frequency amplifier, and fed to a phase-sensitive 'lock-in' amplifier (Dicke 1946) in which it is mixed at a second detector with a voltage of the same frequency obtained directly from the supply energizing the sweep coils. The d.c. output from the second detector is read on a meter. Provided the resonance curve may be considered straight over the region covered by the sweep (and in the absence of saturation effects) a graph of the output meter reading against magnetic field is the differential of the resonance curve. The method is highly sensitive and is not affected by the frequency response of the amplifiers.

The main magnetic field was produced by an electromagnet energized by a battery of accumulators. Its poles were shaped to give a uniform field at the specimen, which had a volume of about 1 cm³. The small variations of magnet current required for the plotting of a resonance curve were measured by a potentiometer method. To calibrate the potentiometer system in terms of magnetic field, use was made of the ^{19}F resonance which at the frequency used is separated from the ^{1}H resonance by 125 gauss. The ^{19}F resonance was provided by the coil formers, which were made of P.T.F.E. (polytetrafluorethylene)* to avoid the possibility of proton resonance from the formers.

In order to make relaxation measurements, and also to allow time for thermal equilibrium to be established in the specimen in regions of high specific heat, it was desirable to keep the temperature of the specimen constant within 1° C over periods of about 1 hour. Adequate control of the temperature was secured by an apparatus operating on the 'heat leak' principle (Alpert 1949). The specimen and coils were surrounded by a copper can 2 mm thick which was screwed to a copper block connected by a heat conducting rod to a bath of liquid oxygen. A heating coil was wound non-inductively on the copper block, and the whole system was surrounded by a Dewar vessel. By varying the power supplied to the heating coil the temperature of the block and can could be held at any temperature between room temperature and liquid oxygen temperature. The equilibrium time was about half an hour, and about 10 watts heating was required to maintain the highest temperature used, 290° K. The temperature of the specimen was measured by a copper–constantan thermocouple having one junction mounted close to the specimen and the other in melting ice. For checking and control purposes other thermojunctions were fixed to the copper block and at the bottom of the copper can.

§ 3. RESULTS

(i) *The Ammonium Halides*

The ammonium halides were investigated in view of the possibility of changes in the proton magnetic resonance associated with the λ-anomalies in their specific heats, discovered by Simon, von Simson and Ruhemann (1927). Our results are in substantial agreement with those of Gutowsky and Pake (1948) and Sachs and Turner (see Purcell 1951).

The structure of the ammonium halides is cubic, each cube of eight halogens having a nitrogen atom at its centre, with the four hydrogen atoms disposed about it in a tetrahedron. Pauling (1930) suggested that the anomaly in the specific heat of each salt is due to the onset of rotation of the tetrahedron of hydrogens about the nitrogen. Such a rotation would reduce the width of the proton resonance line. Frenkel (1935) on the other hand suggested that the tetrahedra are not capable of free rotation, but of oscillation about the nitrogen atom, the axes of oscillation being ordered in space below the λ point, while above it their directions are disordered. Such a change would have no marked effect on the nuclear resonance. Frenkel's theory was supported by the experiments of Lawson (1940) who from measurements of the elastic constants of ammonium chloride was able to derive the value of the specific heat at constant volume from the results of Simon, von Simson and Ruhemann. He found that the specific heat both above and below the transition is approximately 18 cal/deg mole, consistent with the attribution of 12 cal/deg mole to lattice vibration and 6 cal/deg mole to three oscillational degrees of freedom of the hydrogen tetrahedron. Measurements were made on ammonium chloride, ammonium bromide and ammonium iodide. In no case was any discontinuity

* This material was kindly supplied by Messrs I.C.I. Plastics.

found in either the width of the nuclear resonance line or the relaxation time at the λ-point, but line width transitions were observed at very much lower temperatures. The line width in ammonium bromide fell from 25 gauss to 5·0 gauss as the temperature rose above 99° K, and in the chloride from 25 gauss to 5·3 gauss above 128° K. (These temperatures are somewhat below those given by Gutowsky and Pake (1948), viz. 108° K and 135° K respectively.) In ammonium iodide the line showed some sign of broadening at the lowest temperature reached, 78° K; the transition is probable at about 73° K. A graph of line width, defined as the separation of the maximum and minimum of the differentiated absorption curve, for the bromide is given in fig. 1.

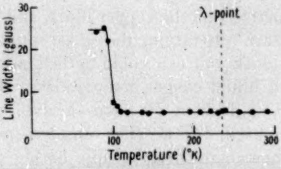

Fig. 1. Line width of proton magnetic resonance in ammonium bromide plotted against temperature.

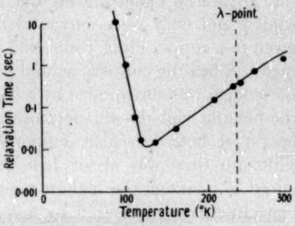

Fig. 2. Spin–lattice relaxation time for proton magnetic resonance in ammonium bromide plotted against temperature.

To obtain quantitative information on the nuclear magnetic interaction it is necessary to determine the shape of the whole absorption curve, from which the mean square width of the resonance line can be calculated. The mean square width of the proton resonance from ammonium bromide at 90° K is 52 gauss^2, consistent with the ammonium ions being stationary. Assuming a lattice spacing of 4·0 Å between like ions (Bartlett and Langmuir 1921) we deduce a N–H distance of $1{\cdot}03 \pm 0{\cdot}01$ Å. This may be compared with the values $1{\cdot}025 \pm 0{\cdot}005$ Å from nuclear resonance (Gutowsky, Kistiakowsky, Pake and Purcell 1949) and the values from neutron diffraction measurements on deuterated ammonium salts, $1{\cdot}03 \pm 0{\cdot}02$ Å for the chloride (Goldschmidt and Hurst 1951) and $0{\cdot}99 \pm 0{\cdot}02$ for the bromide (Levy and Peterson 1951). Above the transition, at 137° K, the mean square width in ammonium bromide is 3·6 gauss^2, indicating that rotational motion of the ammonium ion is sufficiently rapid to render interactions between protons in the same ion ineffective. A mean square width of 3·2 gauss^2 is given by an approximate calculation of the mean square interaction field of protons in neighbouring ions, averaged over all possible positions, made by assuming that the protons move independently over spherical surfaces centred on the nitrogen atoms.

A frequency of rotation sufficient to narrow the nuclear resonance may yet have no influence on the thermal properties of a substance. An estimate of the rate of rotation may be obtained from observations of the relaxation time T_1. Figure 2 shows the variation of the relaxation time of ammonium bromide with temperature. Assuming that the relaxation time is governed by molecular motion, the following relation was obtained by Bloembergen (1948) between the relaxation time T_1 and the characteristic time τ_c of molecular motion:

$$\frac{1}{T_1} = K_1 \left[\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{2\tau_c}{1+4\omega^2\tau_c^2} \right].$$

In this relation, $\omega/2\pi$ is the frequency of measurement and the constant K_1 depends on internuclear distances and nuclear moments. We may determine K_1 from the fact that the minimum in the curve of T_1 against temperature must correspond to the minimum in the relation between T_1 and τ_c. Values of τ_c obtained between temperatures of 90° K and 290° K then fit approximately the relation $1/\tau_c = 2{\cdot}5 \times 10^{13} \exp(-1\,800/T)$. This type of formula fits the supposition that the rotation of the ammonium ion is hindered (Gutowsky and Pake 1950), an energy ϵ being required to cross the barrier to rotation. The probability of the ion crossing the barrier is then proportional to $\exp(-\epsilon/\boldsymbol{k}T)$. A characteristic temperature of 1 800° K corresponds to a barrier of 3 500 cal/mole.

Measurements were also made of the variation of relaxation time with temperature for ammonium iodide. Our results on this salt are less complete, but the general behaviour is similar to that of the bromide. The minimum relaxation time of 0·05 sec occurs at approximately 100° K. The barrier to rotation could only be calculated very approximately at 1 700 to 2 200 cal/mole. Discontinuities in the line width and relaxation time were found at the first-order phase transition of this salt, which occurs at 255° K, the line width increasing from 4·5 to 5·8 gauss and the relaxation time increasing from 1·3 to approximately 20 seconds. Measurements of relaxation time in the chloride were made only at temperatures near the λ-point (243° K). They showed that the relaxation time is increasing with rise of temperature in this region, and that there is no discontinuity at the λ-point. All the evidence is then consistent with the view that in these salts a hindered rotation occurs at a rate increasing with temperature, but much too low to contribute appreciably to the specific heat at temperatures of the order of the λ-points.

(ii) *Methyl Alcohol*

Methyl alcohol has a λ-anomaly in the specific heat at 157·4° K (Kelley 1929) and a sharp change in the dielectric constant at about 160° K (Smyth and McNeight 1936) which might be connected with the onset of rotation of the CH_3OH molecules or part of them.

The results of measurements of the proton line width between 77° K and 290° K are shown in fig. 3. The line width remained constant at about 4·5 gauss from 77° K to just below the λ-point. Above the λ-point the line width was so small as to be limited by the inhomogeneities of the magnetic field (0·1 gauss). The line width transition took the form not of a steady decrease of the line width as the temperature was raised, but of a gradual replacement of the wide line by a narrow one. The narrow line first became detectable at 145° K, and became more prominent as the temperature was increased until at 156° K the wide line could no longer be detected. The results for the width of the wide component just below the λ-point are rather scattered, and there is probably no significance in the apparent slight increase of line width. Line width measurements in this region of temperature were difficult owing to the long relaxation time, which necessitated the use of very small radio-frequency fields.

To obtain more information on the progress of the transition as the temperature was raised, some measurements were made of the variation with temperature of the amplitude of the narrow component. The results shown in fig. 4 were obtained using a radio-frequency field of amplitude $2H_1 = 0{\cdot}008$ gauss, and a sweep field $H_s = 0{\cdot}48$ gauss. Under these conditions the line-width of the narrow component was entirely determined by the sweep field, and H_1 was small enough to avoid saturation effects. The variation of spin–lattice relaxation time with temperature is shown in fig. 5. The results between 110° K and 157° K are rather inaccurate, as the saturation method did not yield well-defined values for the relaxation time.

The line width of 4·5 gauss below the λ-point is too small to be accounted for on the assumption that the methyl alcohol molecules are completely stationary. The CH_3 group at least must have some freedom of rotation, for the assumption of stationary CH_3 groups would yield a line of second moment at least 22 gauss^2, whereas measurements of this quantity at 90° K gave values between 5 and 10 gauss^2. (The inaccuracy in the experimental value arises from the shape of the resonance curves, which tail off very slowly at each side.) The relaxation process below the λ-point is presumably largely due to this motion.

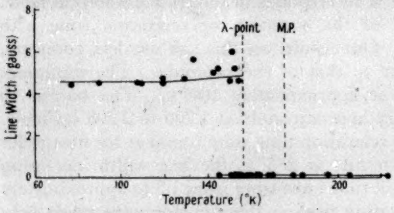

Fig. 3. Line width of proton magnetic resonance in methyl alcohol plotted against temperature.

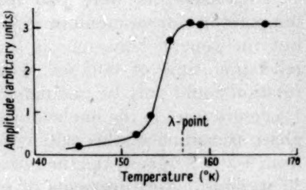

Fig. 4. Amplitude, in arbitrary units, of narrow component of proton magnetic resonance line in methyl alcohol plotted against temperature.

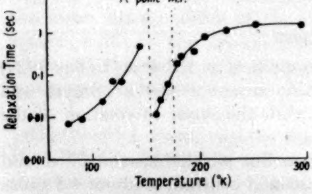

Fig. 5. Spin–lattice relaxation time for proton magnetic resonance in methyl alcohol plotted against temperature.

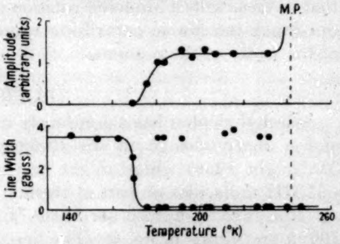

Fig. 6. Upper curve: amplitude, in arbitrary units, of narrow component of proton magnetic resonance line in dimethyl sulphate plotted against temperature.
Lower curve: line width of the resonance plotted over the same range of temperature.

The complete transformation of the character of the proton resonance at the λ-point indicates a considerable change in the rate of molecular motion in solid methyl alcohol at this temperature. The extremely narrow line present between the λ-point and the melting point could not be accounted for by independent rotation of the molecules about fixed centres. It is remarkable that the (relaxation time–temperature) curve is continuous through the melting point, indicating that the molecular motion responsible for nuclear spin relaxation in the solid just below the melting point is little different from that in the liquid.

Similar conclusions were reached for solid hydrogen (Hatton and Rollin 1949), and for methane (Thomas, Alpert and Torrey 1950).

It may be noted that our results do not agree with those of Gutowsky and Pake (1950) who obtained a line width of 8·5 gauss in the solid state with no change at the λ-point. It is difficult to account for this discrepancy. The temperature control is believed to have been better in the present experiments than in those of Gutowsky and Pake, in which there may not have been time for the transition to take place, but this would not account for the difference in line width below the λ-point. Gutowsky and Pake found that the line width is considerably affected by impurities. The chief difficulty is removing water. The specimen we used, which was kindly supplied to us by Dr. D. V. Clifton of the Dyson Perrins Laboratory, Oxford, had been dried by the method of Bjerrum and Zechmeister (1923). The melting point was 176·0 ± 0·3° K. Moreover, a subsidiary experiment made on a specimen containing a few per cent of water gave exactly the same line width at 90° K. Later measurements have shown that the measurement of line width in terms of the separation of the maximum and minimum of the differentiated absorption curves is not entirely satisfactory, the line width so measured increasing as the amplitude of the radio-frequency field is decreased.

(iii) *Dimethyl Sulphate*

Dimethyl sulphate shows an interesting transition in the dielectric constant at 203° K (Smyth and Hitchcock 1932), suggesting some freedom of molecular movement above this temperature. The melting point is 242° K leaving a considerable temperature range for observations between the transition and melting points.

The measured variation of line width with temperature is shown in fig. 6. It remains constant at 3·4 gauss up to about 170° K, when it decreases quite sharply to zero. Results in the transition region were extremely difficult to obtain owing to time or hysteresis effects. Above 175° K the resonance line consisted of two parts, a very narrow component and a component of the same width as below the transition. The variation with temperature of the amplitude of the narrow component is also shown in fig. 6, for the conditions $H_1 = 0{\cdot}008$ gauss, $H_s = 0{\cdot}5$ gauss. There is no change at the dielectric transition point (203° K), the amplitude remaining constant from 190° K to the melting point, where it increases by a factor of ten.

Relaxation measurements were not attempted except in the region below the transition. The relaxation time decreased as the temperature fell (0·6 sec at 125° K, 0·14 sec at 77° K).

The line width below the transition is small enough to suggest that at least the methyl groups are rotating. Above the transition a more violent motion must occur, as in methyl alcohol.

§ 4. CONCLUSION

The variation of proton magnetic resonance line width has now been investigated in a number of materials. It appears that the rotation of the molecules in the solid state does not usually begin at a λ-point or first-order transition, but that the rate of rotation generally increases steadily with temperature. Thus many substances are potentially interesting with regard to their nuclear resonance behaviour, and not merely those which show specific heat anomalies. In some cases it has proved possible to relate the variation of the rate of rotation to a potential barrier. The correlation between evidence from nuclear line widths and from observations of dielectric constants is poor. The proton lines observed in many organic substances at the temperature of liquid oxygen are narrow enough to indicate molecular rotation at frequencies greater than 100 kc/s, whereas dielectric constant measurements do not.

The very narrow lines observed in many substances present a difficulty of interpretation. They can occur only if the fluctuating magnetic field at one nucleus due to all its neighbours averages very nearly to zero. It is at least required that the field changes sign as a result of the motion. If neighbouring molecules are moving independently, the radii joining pairs of protons in neighbouring molecules must turn through angles of at least 90°, which is not in general possible as a result of molecular rotation about fixed centres. It may be necessary to consider some other relative motion of molecules, such as self-diffusion.

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REFERENCES

Alpert, N. L., 1949, *Phys. Rev.*, **75**, 398.
Andrew, E. R., 1950, *J. Chem. Phys.*, **18**, 607.
Bartlett, G., and Langmuir, I., 1921, *J. Amer. Chem. Soc.*, **43**, 84.
Bitter, F., Alpert, N. L., Poss, H. L., Lehr, C. G., and Lin, S. T., 1947, *Phys. Rev.*, **71**, 738.
Bjerrum, N., and Zechmeister, L., 1923, *Ber. dtsch. Chem. Ges.* B, **56**, 894.
Bloch, F., Hansen, W. W., and Packard, M., 1946, *Phys. Rev.*, **70**, 474.
Bloembergen, N., 1948, *Nuclear Magnetic Relaxation* (The Hague: Martinivs Nijhoff).
Bloembergen, N., Purcell, E. M., and Pound, R. V., 1948, *Phys. Rev.*, **73**, 679.
Dicke, R. H., 1946, *Rev. Sci. Instrum.*, **17**, 268.
Frenkel, J., 1935, *Acta Phys.*, **3**, 23.
Goldschmidt, G. H., and Hurst, D. G., 1951, *Phys. Rev.*, **83**, 88.
Gutowsky, H. S., 1951, *Phys. Rev.*, **83**, 1073.
Gutowsky, H. S., Kistiakowsky, G. B., Pake, G. E., and Purcell, E. M., 1949, *J. Chem. Phys.*, **17**, 972.
Gutowsky, H. S., and Pake, G. E., 1948, *J. Chem. Phys.*, **16**, 1164; 1950, *Ibid.*, **18**, 162.
Hatton, J., and Rollin, B. V., 1949, *Proc. Roy. Soc.* A, **199**, 222.
Kelley, K. K., 1929, *J. Amer. Chem. Soc.*, **51**, 180.
Lawson, A. W., 1940, *Phys. Rev.*, **57**, 417, 559.
Levy, H. A., and Peterson, S. W., 1951, *Phys. Rev.*, **83**, 1270.
Norberg, R. E., and Schlichter, C. P., 1951, *Phys. Rev.*, **83**, 1074.
Pauling, L., 1930, *Phys. Rev.*, **36**, 430.
Purcell, E. M., 1951, *Physica*, **17**, 282.
Purcell, E. M., Torrey, H. C., and Pound, R. V., 1946, *Phys. Rev.*, **69**, 37.
Rabi, I. I., Zacharias, J. R., Millman, S., and Kusch, P., 1938, *Phys. Rev.*, **53**, 318.
Simon, F., von Simson, C., and Ruhemann, M., 1927, *Z. Phys. Chem.*, **129**, 339.
Smyth, C. P., and Hitchcock, C. S., 1932, *J. Amer. Chem. Soc.*, **54**, 631.
Smyth, C. P., and McNeight, S. A., 1936, *J. Amer. Chem. Soc.*, **58**, 597.
Thomas, J. T., Alpert, N. L., and Torrey, H. C., 1950, *J. Chem. Phys.*, **18**, 1511.
Van Vleck, J. H., 1948, *Phys. Rev.*, **74**, 168.

The Two-Band Effect in Conduction

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ABSTRACT. For an isotropic two-band conductor in a transverse magnetic field, the various galvanomagnetic, thermomagnetic and thermoelectric coefficients are derived by elementary arguments in terms of those of the individual bands. The expressions are applicable to quasi-free electrons of any degree of degeneracy : for fully degenerate electrons they reduce to those already given by Sondheimer and Wilson. When the square of the thermoelectric power is comparable with the Lorenz number, as may happen in semiconductors, the expressions for the adiabatic thermomagnetic and thermoelectric effects become extremely complicated, though those for the isothermal effects remain reasonably simple.

§ 1. INTRODUCTION

In extending the electron theory of metals and semiconductors beyond the point represented by the simple free-electron model, a number of authors have studied the properties of a model consisting of two non-interacting bands of electrons. In particular, the behaviour of such a model in a transverse magnetic field has been studied in some detail, because it is qualitatively different from that of the simpler model, and because it represents more closely the behaviour observed in real conductors. We may mention the work of Riecke (1898), Fowler (1936), Jones (1936), Kohler (1949 a–d), and Klahr (1951), and in particular of Sondheimer and Wilson (1947) and Sondheimer (1948), hereafter referred to as S–W and S respectively. These last authors have considered a model consisting of two isotropic bands of degenerate quasi-free electrons and have given expressions which are approximately valid at all temperatures, including the region of the Debye temperature, for the electrical and thermal conductivities, and the various thermoelectric, thermomagnetic and galvanomagnetic effects, in a transverse magnetic field. These results were obtained by first finding 'interpolation formulae' for the properties of a *single* band in a transverse field, which reduced to the known correct expressions for temperatures well above and well below the Debye temperature, and then evaluating the properties of the two-band model in terms of these formulae.

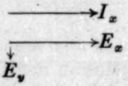
It is clear from the nature of the two-band model that it must be possible to express its properties quite generally in terms of those of the individual bands, since for given fields, the currents flowing in a two-band conductor are simply the vector sums of those produced by these fields in the individual bands. For degenerate quasi-free electrons, the results are implicit in the work of Sondheimer and Wilson, but their simple nature is somewhat obscured by the mathematical details of the 'interpolation formulae'. In the present paper we give a brief derivation of the general expressions, applicable to any isotropic two-band conductor of any degree of degeneracy. In deriving these expressions it is convenient to make use of certain relations which are considered in the next section.

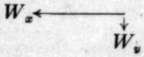
§ 2. DEFINITIONS. THE HEURLINGER RELATIONS

Consider an isotropic conductor, in a uniform magnetic field H directed along the z axis, in which is flowing a longitudinal current, electrical or thermal, of density I_x or W_x. Then there are four main experimental arrangements to consider. In all of them, the transverse electrical current is zero: $I_y=0$. In two of them the primary current is electrical, and in two thermal. In one electrical and in one thermal arrangement, the transverse temperature gradient is zero: $\partial T/\partial y=T_y'=0$ (isothermal arrangements); in the other cases, the transverse heat flow is zero: $W_y=0$ (adiabatic arrangements). These four arrangements, and the parameters defined by them, are classified below. In the vector diagrams, the various secondary fields and currents are shown having the signs they will have for an ideal free-electron metal, according to Kohler (1941 a), if the field H_z is positive, i.e. directed out of the paper towards the reader. Thus for type I, E_y is shown as negative, because the Hall coefficient A_{H} is negative for a free-electron metal.

Isothermal Arrangements $I_y=T_y'=0$

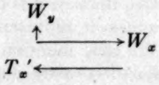
Type I. $T_x'=0$

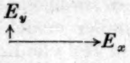




$$I_x/E_x=\sigma^{\mathrm{i}}, \qquad E_y/HI_x=A^{\mathrm{i}}_{\mathrm{H}}, \qquad W_x/I_x=\mu^{\mathrm{i}}_W.$$

Type II. $I_x=0$

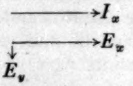


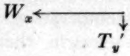


$$-W_x/T_x'=\kappa^{\mathrm{i}}, \qquad -E_y/HT_x'=B^{\mathrm{i}}_{\mathrm{EN}}, \qquad E_x/T_x'=\mu^{\mathrm{i}}_E.$$

Adiabatic Arrangements $I_y=W_y=0$

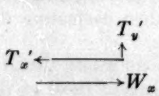
Type III. $T_x'=0$

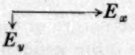




$$I_x/E_x=\sigma^{\mathrm{a}}, \qquad E_y/HI_x=A^{\mathrm{a}}_{\mathrm{H}}, \qquad -T_y'/HI_x=A_{\mathrm{E}}, \qquad W_x/I_x=\mu^{\mathrm{a}}_W.$$

Type IV. $I_x=0$





$$-W_x/T_x'=\kappa^{\mathrm{a}}, \qquad -E_y/HT_x'=B^{\mathrm{a}}_{\mathrm{EN}}, \qquad T_y'/HT_x'=B_{\mathrm{RL}}, \qquad E_x/T_x'=\mu^{\mathrm{a}}_E.$$

These four arrangements thus suffice to define the isothermal and adiabatic electrical and thermal conductivities, σ and κ, Hall and Ettinghausen–Nernst coefficients A_{H} and B_{EN}, and 'Thomson coefficients' μ_W and μ_E, and the Ettinghausen and Righi–Leduc coefficients A_{E} and B_{RL}. Now it is obvious from the vector diagrams that types II and IV differ only by a slight relative rotation of the x and y axes, and that type I can be constructed from type III by superposing a small field of type II in the y direction. It follows that among the numerous coefficients defined above, relatively few are independent, and in fact the following relations must hold ($\rho = 1/\sigma$):

$$\rho^{\mathrm{a}} = \rho^{\mathrm{i}} - B^{\mathrm{i}}{}_{\mathrm{EN}} A_{\mathrm{E}} H^2, \qquad \ldots\ldots(1)$$

$$\kappa^{\mathrm{a}} = \kappa^{\mathrm{i}}(1 + B_{\mathrm{RL}}{}^2 H^2), \qquad \ldots\ldots(2)$$

$$A^{\mathrm{a}}{}_{\mathrm{H}} = A^{\mathrm{i}}{}_{\mathrm{H}} - \mu^{\mathrm{i}}{}_E A_{\mathrm{E}}, \qquad \ldots\ldots(3)$$

$$B^{\mathrm{a}}{}_{\mathrm{EN}} = B^{\mathrm{i}}{}_{\mathrm{EN}} - \mu^{\mathrm{i}}{}_E B_{\mathrm{RL}}, \qquad \ldots\ldots(4)$$

$$\mu^{\mathrm{a}}{}_E = \mu^{\mathrm{i}}{}_E + B^{\mathrm{i}}{}_{\mathrm{EN}} B_{\mathrm{RL}} H^2, \qquad \ldots\ldots(5)$$

$$\mu^{\mathrm{a}}{}_W = \mu^{\mathrm{i}}{}_W + \kappa^{\mathrm{i}} B_{\mathrm{RL}} A_{\mathrm{E}} H^2, \qquad \ldots\ldots(6)$$

also

$$W_y(\mathrm{I}) = -\kappa^{\mathrm{i}} A_{\mathrm{E}} H I_x, \qquad \ldots\ldots(7)$$

$$W_y(\mathrm{II}) = \kappa^{\mathrm{i}} B_{\mathrm{RL}} H T'_x. \qquad \ldots\ldots(8)$$

These relations are necessarily valid for any conductor (two-band as well as one-band) which in a field H_z remains isotropic in the xy plane. They are thus applicable for instance to a conductor of cubic symmetry, if z is a tetrad axis, as well as to free-electron models. They can obviously be generalized immediately to anisotropic conductors, provided that H is directed along a principal axis, but not so readily otherwise. They were first given by Heurlinger (1915, 1916); they have also been derived recently, in the course of an analysis of the problem by the methods of Onsager thermodynamics, by Mazur and Prigogine (1951) and by Callen (1952). We shall refer to them as the Heurlinger relations.

The coefficients μ_E and μ_W which appear in eqns. (3) to (6) are of less interest in practice than the thermoelectric power ϵ and the Peltier coefficient Π of the material. For any conductor, these are related to μ_E and μ_W by

$$\mu_E = \epsilon - \frac{1}{e}(d\zeta/dT), \qquad \ldots\ldots(9)$$

$$\mu_W = \Pi - \zeta/e, \qquad \ldots\ldots(10)$$

where $-e$ is the electronic charge and ζ the chemical potential of an electron, so that we may at once replace (5) and (6) by

$$\epsilon^{\mathrm{a}} = \epsilon^{\mathrm{i}} + B^{\mathrm{i}}{}_{\mathrm{EN}} B_{\mathrm{RL}} H^2, \qquad \ldots\ldots(5\,a)$$

$$\Pi^{\mathrm{a}} = \Pi^{\mathrm{i}} + \kappa^{\mathrm{i}} B_{\mathrm{RL}} A_{\mathrm{E}} H^2. \qquad \ldots\ldots(6\,a)$$

Now consider eqns. (3) and (4). It was pointed out by Heurlinger that $A^{\mathrm{a}}{}_{\mathrm{H}}$ and $B^{\mathrm{a}}{}_{\mathrm{EN}}$ cannot be measured directly, but that the observations must be corrected for the thermoelectric e.m.f. in the leads (cf. also Kohler 1941 c). If, however, this e.m.f. is calculated in the usual way as $\int \epsilon\, dT$ rather than as $\int \mu_E\, dT$, the quantities $A^{\mathrm{a}}{}_{\mathrm{H}}$ and $B^{\mathrm{a}}{}_{\mathrm{EN}}$ so obtained will not be those defined above, but will be given by

$$A^{\mathrm{a}}{}_{\mathrm{H}} = A^{\mathrm{i}}{}_{\mathrm{H}} - \epsilon^{\mathrm{i}} A_{\mathrm{E}}, \qquad \ldots\ldots(3\,a)$$

$$B^{\mathrm{a}}{}_{\mathrm{EN}} = B^{\mathrm{i}}{}_{\mathrm{EN}} - \epsilon^{\mathrm{i}} B_{\mathrm{RL}}. \qquad \ldots\ldots(4\,a)$$

The two alternative definitions of $B^{\mathrm{a}}{}_{\mathrm{EN}}$ corresponding to (4) and (4 *a*) have been used respectively by Kohler (1941 a, b), whose expressions satisfy eqn. (4), and Sondheimer (1948), whose equation (39) corresponds to our equation (4 *a*). Since we shall be concerned with deriving generalizations of Sondheimer's expressions, we shall henceforth adopt the definitions of $A^{\mathrm{a}}{}_{\mathrm{H}}$ and $B^{\mathrm{a}}{}_{\mathrm{EN}}$ corresponding to eqns. (3 *a*) and (4 *a*).

In addition to the above relations, the coefficients Π and ϵ are related by the second Thomson relation:

$$\Pi^{\mathrm{i}}=T\epsilon^{\mathrm{i}};\qquad \Pi^{\mathrm{a}}=T\epsilon^{\mathrm{a}}, \qquad \ldots\ldots(11)$$

and finally, combining (5 *a*), (6 *a*), and (11), we obtain the Bridgman relation:

$$B^{\mathrm{i}}_{\mathrm{EN}}T=\kappa^{\mathrm{i}}A_{\mathrm{E}}. \qquad \ldots\ldots(12)$$

Equations (11) and (12) have been obtained by Meixner (1939, 1941) and Kohler (1941 c) using the electron theory of metals, and thermodynamically by Callen (1948) and Mazur and Prigogine (1951) using the Onsager reciprocal relations.

In considering the two-band conductor, it is easiest to derive the isothermal coefficients; the adiabatic coefficients may then be found from them with the help of the above relations.

§ 3. THE TWO-BAND CONDUCTOR

From now on we shall usually be concerned with isothermal values of σ and A_{H}, and the superscript i will be dropped; where the quantities σ^{a}, $A^{\mathrm{a}}_{\mathrm{H}}$ occur they will be so written.

Consider a conductor containing two isotropic, independent bands of conduction electrons, whose individual properties we shall denote by subscripts 1 and 2. Then both bands will necessarily be subjected to the same electric fields and temperature gradients, but the resultant electrical and thermal currents in the individual bands will not in general have the same magnitude, and unless $A_{\mathrm{H},1}\sigma_1=A_{\mathrm{H},2}\sigma_2$ and $B_{\mathrm{RL},1}=B_{\mathrm{RL},2}$ they will not have the same direction. The two-band effects arise simply because the total electrical and thermal currents in the conductor are then the vector sums of those in the individual bands, rather than the algebraic sums, so that, for instance, if the total transverse current is zero, the transverse currents in the individual bands will be not zero but equal and opposite. If $A_{\mathrm{H},1}\sigma_1=A_{\mathrm{H},2}\sigma_2$ and $B_{\mathrm{RL},1}=B_{\mathrm{RL},2}$, so that the angles between field and current are the same in both bands, the generalizations introduced by the two-band model vanish.

The properties of either band individually, or of the conductor as a whole (denoted by subscript 3) may be represented by equations of the form

$$\left.\begin{aligned} I_x&=\alpha_{\mathrm{A}}E_x+\alpha_{\mathrm{B}}E_y+\alpha_{\mathrm{C}}T_x'+\alpha_{\mathrm{D}}T_y' \\ I_y&=-\alpha_{\mathrm{B}}E_x+\alpha_{\mathrm{A}}E_y-\alpha_{\mathrm{D}}T_x'+\alpha_{\mathrm{C}}T_y' \\ W_x&=\beta_{\mathrm{A}}E_x+\beta_{\mathrm{B}}E_y+\beta_{\mathrm{C}}T_x'+\beta_{\mathrm{D}}T_y' \\ W_y&=-\beta_{\mathrm{B}}E_x+\beta_{\mathrm{A}}E_y-\beta_{\mathrm{D}}T_x'+\beta_{\mathrm{C}}T_y' \\ I_z,\ W_z&=f(E_z,\ T_z')\ \text{only,} \end{aligned}\right\} \qquad \ldots\ldots(13)$$

and if we write

$$A_{\mathrm{H}}\sigma H=t \qquad \ldots\ldots(14), \qquad\qquad \sigma/(1+t^2)=\phi \qquad \ldots\ldots(15)$$

it is easily shown that the following relations hold between the coefficients α, β and the quantities defined in § 2:

$$\left.\begin{aligned} &\alpha_{\mathrm{A}}=\phi, \qquad\qquad \alpha_{\mathrm{B}}=\phi t, \\ &\alpha_{\mathrm{C}}=-\phi(\mu^{\mathrm{i}}_{E}-B^{\mathrm{i}}_{\mathrm{EN}}Ht), \qquad \alpha_{\mathrm{D}}=-\phi(\mu^{\mathrm{i}}_{E}t+B^{\mathrm{i}}_{\mathrm{EN}}H), \\ &\beta_{\mathrm{A}}=\phi(\mu^{\mathrm{i}}_{W}-\kappa^{\mathrm{i}}A_{\mathrm{E}}Ht), \qquad \beta_{\mathrm{B}}=\phi(\mu^{\mathrm{i}}_{W}t+\kappa^{\mathrm{i}}A_{\mathrm{E}}H), \\ &\beta_{\mathrm{C}}=-\kappa^{\mathrm{i}}+\phi[(\mu^{\mathrm{i}}_{W}t+\kappa^{\mathrm{i}}A_{\mathrm{E}}H)B^{\mathrm{i}}_{\mathrm{EN}}H-(\mu^{\mathrm{i}}_{W}-\kappa^{\mathrm{i}}A_{\mathrm{E}}Ht)\mu^{\mathrm{i}}_{\mathrm{E}}], \\ &\beta_{\mathrm{D}}=-\kappa^{\mathrm{i}}B_{\mathrm{RL}}H-\phi[(\mu^{\mathrm{i}}_{W}t+\kappa^{\mathrm{i}}A_{\mathrm{E}}H)\mu^{\mathrm{i}}_{E}+(\mu^{\mathrm{i}}_{W}-\kappa^{\mathrm{i}}A_{\mathrm{E}}Ht)B^{\mathrm{i}}_{\mathrm{EN}}H]. \end{aligned}\right\} \qquad \ldots\ldots(16)$$

The properties of the two-band conductor are now given at once, in terms of those of the individual bands, by the set of equations

$$\alpha_3=\alpha_1+\alpha_2, \qquad \beta_3=\beta_1+\beta_2. \qquad \ldots\ldots(17)$$

Moreover, using (9) and (10) in eqn. (17), it is easily seen that the terms in ζ, $d\zeta/dT$ always cancel, so that if we define α', β' from α, β by replacing $\mu^{\mathrm{i}}{}_{E}$ and $\mu^{\mathrm{i}}{}_{W}$ everywhere by ϵ^{i}, $T\epsilon^{\mathrm{i}}$, eqns. (17) become

$$\alpha_3'=\alpha_1'+\alpha_2', \qquad \beta_3'=\beta_1'+\beta_2'. \qquad \ldots\ldots(17\,a)$$

[It may be noted that for a degenerate free-electron model, S–W, eqns. (20) and (22), and S, eqn. (2), define quantities V, W, X, Y, P and Q related to our α', β' by

$$\left.\begin{aligned} &V=C\alpha'_{\mathrm{A}}/\mathbf{e}^2,\;\; W=-C\alpha'_{\mathrm{B}}/\mathbf{e}^2,\;\; X=-C\beta'_{\mathrm{C}}/\boldsymbol{k}^2T,\;\; Y=C\beta'_{\mathrm{D}}/\boldsymbol{k}^2T,\\ &P=C\alpha'_{\mathrm{C}}/\boldsymbol{k}^2T\mathbf{e}=-C\beta'_{\mathrm{A}}/\boldsymbol{k}^2T^2\mathbf{e},\;\; Q=-C\alpha'_{\mathrm{D}}/\boldsymbol{k}^2T\mathbf{e}=C\beta'_{\mathrm{B}}/\boldsymbol{k}^2T^2\mathbf{e} \end{aligned}\right\} \qquad \ldots\ldots(18)$$

where $C=3\pi^2\hbar^4$.]

From (16) and (17 *a*) the parameters of the two-band model at once follow in terms of those of the individual bands. For instance, from α'_{A} and α'_{B} we have

$$\phi_3=\phi_1+\phi_2, \qquad \phi_3t_3=\phi_1t_1+\phi_2t_2, \qquad \ldots\ldots(19)$$

which give, using (14) and (15), the expressions

$$\sigma_3=\frac{(\sigma_1+\sigma_2)^2+\sigma_1{}^2\sigma_2{}^2H^2(A_{\mathrm{H},1}+A_{\mathrm{H},2})^2}{\sigma_1+\sigma_2+\sigma_1\sigma_2H^2(\sigma_1A_{\mathrm{H},1}{}^2+\sigma_2A_{\mathrm{H},2}{}^2)}, \qquad \ldots\ldots(20)$$

and

$$A_{\mathrm{H},3}=\frac{\sigma_1{}^2A_{\mathrm{H},1}+\sigma_2{}^2A_{\mathrm{H},2}+\sigma_1{}^2\sigma_2{}^2H^2A_{\mathrm{H},1}A_{\mathrm{H},2}(A_{\mathrm{H},1}+A_{\mathrm{H},2})}{(\sigma_1+\sigma_2)^2+\sigma_1{}^2\sigma_2{}^2H^2(A_{\mathrm{H},1}+A_{\mathrm{H},2})^2}, \qquad \ldots\ldots(21)$$

which for small H reduces to

$$A_{\mathrm{H},3}=\frac{\sigma_1{}^2A_{\mathrm{H},1}+\sigma_2{}^2A_{\mathrm{H},2}}{(\sigma_1+\sigma_2)^2}.$$

Similarly, from α'_{C} and α'_{D} (or β'_{A} and β'_{B}) we obtain

$$\begin{aligned}\phi_3(1+t_3{}^2)\epsilon^{\mathrm{i}}{}_3=\phi_1[(1+t_1t_3)\epsilon^{\mathrm{i}}{}_1+(t_3-t_1)B^{\mathrm{i}}{}_{\mathrm{EN},1}H]&\\ +\phi_2[(1+t_2t_3)\epsilon^{\mathrm{i}}{}_2+(t_3-t_2)B^{\mathrm{i}}{}_{\mathrm{EN},2}H],& \qquad \ldots\ldots(22)\end{aligned}$$

and

$$\begin{aligned}\phi_3(1+t_3{}^2)B^{\mathrm{i}}{}_{\mathrm{EN},3}H=\phi_1[(1+t_1t_3)B^{\mathrm{i}}{}_{\mathrm{EN},1}H+(t_1-t_3)\epsilon^{\mathrm{i}}{}_1]&\\ +\phi_2[(1+t_2t_3)B^{\mathrm{i}}{}_{\mathrm{EN},2}H+(t_2-t_3)\epsilon^{\mathrm{i}}{}_2],& \qquad \ldots\ldots(23)\end{aligned}$$

for the isothermal thermoelectric power and Ettinghausen–Nernst coefficient of the two-band conductor.

The expressions for β'_{C} and β'_{D} are considerably complicated by the terms in ϕ (cf. eqns. (16)): neglecting these terms for the moment, we obtain relatively simple expressions for $\kappa^{\mathrm{i}}{}_3$ and $B_{\mathrm{RL},3}$, and from these, using (3), (5 *a*), and (12), expressions for the quantities $\kappa^{\mathrm{a}}{}_3$, $\epsilon^{\mathrm{a}}{}_3$ and $A_{\mathrm{E},3}$ may be found from those for $\kappa^{\mathrm{i}}{}_3$, $\epsilon^{\mathrm{i}}{}_3$ and $B^{\mathrm{i}}{}_{\mathrm{EN},3}$. To facilitate comparison with the expressions given by Sondheimer (1948) we have expressed the resulting equations (and also eqn. (23) for $B^{\mathrm{i}}{}_{\mathrm{EN},3}$) in terms of the coefficients σ, A_{H}, κ^{a}, B_{RL}, ϵ^{a} and $\mathrm{B}^{\mathrm{a}}{}_{\mathrm{EN}}$ for the individual bands, eliminating the coefficients ϵ^{i}, $B^{\mathrm{i}}_{\mathrm{EN}}$ and A_{E} by means of the Heurlinger relations. Writing for brevity

$$\begin{aligned}
C_1 &= \kappa^{\mathrm{a}}_1(1+B_{\mathrm{RL},2}{}^2H^2) & C_2 &= \kappa^{\mathrm{a}}_2(1+B_{\mathrm{RL},1}{}^2H^2)\\
C_{12} &= \kappa^{\mathrm{a}}_1(1+B_{\mathrm{RL},1}B_{\mathrm{RL},2}H^2) & C_{21} &= \kappa^{\mathrm{a}}_2(1+B_{\mathrm{RL},1}B_{\mathrm{RL},2}H^2)\\
D_1 &= \kappa^{\mathrm{a}}_1(B_{\mathrm{RL},2}-B_{\mathrm{RL},1})H & D_2 &= \kappa^{\mathrm{a}}_2(B_{\mathrm{RL},1}-B_{\mathrm{RL},2})H\\
S_1 &= \sigma_1{}^2(1+t_2{}^2)+\sigma_1\sigma_2(1+t_1t_2) & S_2 &= \sigma_2{}^2(1+t_1{}^2)+\sigma_1\sigma_2(1+t_1t_2)\\
HV_1 &= \sigma_1\sigma_2(t_1-t_2) & HV_2 &= \sigma_1\sigma_2(t_2-t_1),
\end{aligned}$$

the expressions for the two-band model are:

$$\kappa^{\mathrm{a}}_3=\frac{\kappa^{\mathrm{a}}_1(C_1+C_{21})+\kappa^{\mathrm{a}}_2(C_2+C_{12})}{C_1+C_2}, \qquad \ldots\ldots(24)$$

$$B_{\mathrm{RL},3}=\frac{B_{\mathrm{RL},1}C_1+B_{\mathrm{RL},2}C_2}{C_1+C_2}, \qquad \ldots\ldots(25)$$

$$\begin{aligned}
\epsilon^{\mathrm{a}}_3(S_1+S_2)(C_1+C_2) &= [\epsilon^{\mathrm{a}}_1(C_1+C_{21})-B^{\mathrm{a}}_{\mathrm{EN},1}HD_2]S_1\\
&\quad+[\epsilon^{\mathrm{a}}_1D_2+B^{\mathrm{a}}_{\mathrm{EN},1}H(C_1+C_{21})]HV_2+\ldots \qquad \ldots\ldots(26)
\end{aligned}$$

$$\begin{aligned}
A_{\mathrm{E},3}(S_1+S_2)(C_1+C_2) &= \frac{C_1T}{\kappa^{\mathrm{a}}_1}[(\epsilon^{\mathrm{a}}_1B_{\mathrm{RL},1}+B^{\mathrm{a}}_{\mathrm{EN},1})S_1\\
&\quad+(\epsilon^{\mathrm{a}}_1-B^{\mathrm{a}}_{\mathrm{EN},1}B_{\mathrm{RL},1}H^2)V_1]+\ldots \qquad \ldots\ldots(27)
\end{aligned}$$

$$\begin{aligned}
B^{\mathrm{i}}_{\mathrm{EN},3}(S_1+S_2) &= \frac{\kappa^{\mathrm{a}}_2}{C_2}[(\epsilon^{\mathrm{a}}_1B_{\mathrm{RL},1}+B^{\mathrm{a}}_{\mathrm{EN},1})S_1\\
&\quad+(\epsilon^{\mathrm{a}}_1-B^{\mathrm{a}}_{\mathrm{EN},1}B_{\mathrm{RL},1}H^2)V_1]+\ldots, \qquad \ldots\ldots(28)
\end{aligned}$$

where eqns. (26), (27) and (28) are completed by exactly similar terms with the suffixes 1 and 2 interchanged. For $H=0$ eqn. (26) reduces to

$$\epsilon^{\mathrm{a}}_3=(\sigma_1\epsilon^{\mathrm{a}}_1+\sigma_2\epsilon^{\mathrm{a}}_2)/(\sigma_1+\sigma_2) \qquad \ldots\ldots(28\,a)$$

(cf. Fowler 1936, equation (1241)) which can be derived very simply by considering the equal and opposite longitudinal currents in the individual bands caused by the net excess e.m.f's $(\epsilon^{\mathrm{a}}_3-\epsilon^{\mathrm{a}}_1)$ and $(\epsilon^{\mathrm{a}}_3-\epsilon^{\mathrm{a}}_2)$.

Equations (24) to (27) have been obtained by neglecting the terms in ϕ in the expressions for β'_{C} and β'_{D}. If these terms are retained, the following expressions for κ^{i}_3 and $\kappa^{\mathrm{i}}_3B_{\mathrm{RL},3}$ result:

$$\begin{aligned}
\kappa^{\mathrm{i}}_3 &= \kappa^{\mathrm{i}}_1+\kappa^{\mathrm{i}}_2+\frac{T\sigma_1\sigma_2}{S_1+S_2}[(\Delta\epsilon^2-\Delta B^2H^2)(\sigma_1+\sigma_2)\\
&\quad-2\Delta\epsilon\Delta BH^2\sigma_1\sigma_2(A_{\mathrm{H},1}+A_{\mathrm{H},2})], \qquad \ldots\ldots(29)
\end{aligned}$$

$$\begin{aligned}
\kappa^{\mathrm{i}}_3B_{\mathrm{RL},3} &= \kappa^{\mathrm{i}}_1B_{\mathrm{RL},1}+\kappa^{\mathrm{i}}_2B_{\mathrm{RL},2}+\frac{T\sigma_1\sigma_2}{S_1+S_2}[(\Delta\epsilon^2-\Delta B^2H^2)\sigma_1\sigma_2(A_{\mathrm{H},1}+A_{\mathrm{H},2})\\
&\quad+2\Delta\epsilon\Delta B(\sigma_1+\sigma_2)], \qquad \ldots\ldots(30)
\end{aligned}$$

where $\Delta B=B^{\mathrm{i}}_{\mathrm{EN},1}-B^{\mathrm{i}}_{\mathrm{EN},2}$ and $\Delta\epsilon=\epsilon^{\mathrm{i}}_1-\epsilon^{\mathrm{i}}_2$. The expressions for κ^{a}_3, $B_{\mathrm{RL},3}$, ϵ^{a}_3 and $A_{E,3}$ will correspondingly be a great deal more complicated than those given by eqns. (24) to (27), which are obtained on neglecting the terms in square brackets in (29) and (30). For small magnetic fields, these terms are smaller than the main terms in (29) and (30) by factors of order $\epsilon^2/L_{\mathrm{n}}$, where L_{n} in the Lorenz number, equal to $2{\cdot}24\times10^{-4}$ microvolt² deg⁻². Thus for metals, where ϵ is of order 1–10 μv/degree, the correction terms are always negligible (for a degenerate free-electron model $\epsilon^2/L_{\mathrm{n}}$ is of order $(\boldsymbol{k}T/\zeta)^2$), but for semimetals and semiconductors the correction terms may become comparable with the main terms (e.g. for bismuth, germanium and silicon, ϵ is of order 100–400 μv/degree), and eqns. (24) to (27) must be replaced by the exact expressions derived from (29) and (30). If thermal measurements could be made on semiconductors with $E_x=E_y=0$, rather than $I_x=I_y=0$, these complications would be avoided, but this is probably impracticable.

§ 4. DISCUSSION

With the proviso just mentioned, eqns. (20) to (30) are formally applicable to any two-band conductor, of any degree of degeneracy, to which eqns. (13) are applicable, including not only models consisting of isotropic quasi-free bands of electrons, but also conductors of, for instance, cubic, tetragonal or hexagonal symmetry, if H_z is parallel to the symmetry axis. The generalization to conductors of lower symmetry is straightforward, again provided that H_z is parallel to a principal axis (cf. Jones 1936). If $t_1=t_2$ and $B_{\mathrm{RL},1}=B_{\mathrm{RL},2}$ the characteristic two-band behaviour vanishes, and eqns. (20) and (21), for instance, reduce to $\sigma_3=\sigma_1+\sigma_2$ and $A_{\mathrm{H},3}\sigma_3=A_{\mathrm{H},1}\sigma_1=A_{\mathrm{H},2}\sigma_2$ for all H.

Applied to the model of two quasi-free degenerate bands used by Sondheimer and Wilson, and using for the parameters of the individual bands their interpolation formulae (S–W, eqn. (54); S, eqns. (37), (38), (41), (42)), our equations (20), (21), (24) to (28) become identical with theirs (S–W, eqns. (57), (74); S, eqns. (22), (54) to (57)). Sondheimer (1950 a) has since given the exact evaluation of σ for a single-band free-electron metal in the intermediate temperature region, and has also shown (unpublished) that the exact value of A_{H} in this region is inappreciably different from the value $-1/\boldsymbol{nec}$. These results may be used in (20), (21) to find more accurate values for σ and A_{H} for the two-band model in the intermediate temperature region.

If the parameters of the individual bands vary with H, the values to be used in these equations are of course those appropriate to the applied field. For degenerate free electrons the variation of σ and A_{H} with field is normally negligible, but Sondheimer (1950 b) has found that for a thin film in a transverse field normal to the film, curious oscillations of σ occur with H. Unfortunately they occur only at such high values of H that for any real metal—even for sodium—the normal magneto-resistance effect due to anisotropy would tend to mask them. Using Sondheimer's results for $\sigma(H)$ and $A_{\mathrm{H}}(H)$ for a single band in eqns. (20) and (21), it would at once be possible to evaluate the behaviour of a thin film of the two-band model, and by appropriate choice of the parameters of the model it would be possible to give it the same bulk magneto-resistance behaviour in a transverse field as, say, sodium; but such a model would be a considerable over-simplification (for instance, it would give no longitudinal magneto-resistance effect; the two-band effect, by its nature, cannot do this, whereas in sodium the longitudinal and transverse effects are comparable in size), and it seems doubtful whether it could safely be used for the quantitative evaluation of experimental results on thin films.

For non-degenerate bands, i.e. semiconductors, the values of the parameters of the individual bands will in general vary with the applied field (cf. for example Harding 1933). In low fields, however, the zero-field values of the parameters may be used with, for example, eqn. (21 *a*) to find the zero-field parameters for the two-band model (cf. Fowler 1936, eqn. (1247), Klahr 1951, eqn. (3)). Wright (1951) has made an extensive theoretical investigation of the zero-field parameters of a free-electron conductor of any degree of degeneracy, for various types of mean free path behaviour; his results may at once be extended, using the equations of § 3, to two-band conductors.

It may be noted that the properties of an isotropic single band may be deduced by an extension of the methods of § 3, by regarding it as a continuum of bands, each contributing $d\sigma$ to the total conductivity. Equations (19), for instance, then become $\phi_3 = \int d\phi$, $\phi_3 t_3 = \int t\, d\phi$, and if we put $t = -\mathbf{e}Hl/\mathbf{m}vc$ for quasi-free electrons, and $d\sigma = -(4\pi\mathbf{e}^2 l/3\mathbf{m})v^2(\partial f_0/\partial v)\, dv$, we obtain the usual equations for σ and A_{H} first derived by Gans, and applied with various assumptions concerning $l(v)$ and f_0 by Sommerfeld and Frank (1931), Harding (1933), Klahr (1951) and Wright (1951). Here, as before, the effects of a magnetic field vanish if t is the same for all electrons or if the field is longitudinal, since the effects again arise from the inequality of the Hall effect for the various groups of electrons.

Lastly, we may consider the effect of recombination on the applicability of these equations. Fowler (1936) pointed out that in a transverse magnetic field there will be equal and opposite, non-zero transverse currents in the two bands when the total transverse current is zero, and that in equilibrium the consequent accumulations of charge in the individual bands must be balanced by either recombination or back-diffusion (cf. also Welker 1951). Experimentally it is found that for semiconductors recombination is rapid (Torrey and Whitmer 1948, p. 55) and occurs chiefly at the surface of the conductor (Shockley 1950). In dealing with degenerate two-band models it has generally been tacitly assumed that although the bands are non-interacting, no charge excesses are built up: these assumptions are compatible with the existence of rapid surface recombination. For the results of the present paper to be applicable, it is necessary that recombination shall be rapid, so that the charge excesses in the individual bands remain small enough not to effect their properties: recombination may occur either at the surface or in the volume of the material, provided in the latter case that, in the presence of this interaction, it is still possible to define unambiguously the conduction parameters of the individual bands.

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REFERENCES

CALLEN, H. B., 1948, *Phys. Rev.*, **73,** 1349 ; 1952, *Ibid.*, **85,** 16.
FOWLER, R. H., 1936, *Statistical Mechanics*, 2nd edn. (Cambridge : University Press).
HARDING, J. W., 1933, *Proc. Roy. Soc.* A, **140,** 205.
HEURLINGER, T., 1915, *Ann. Phys., Lpz.*, (4), **48,** 84 ; 1916, *Phys. Z.*, **17,** 221.
JONES, H., 1936, *Proc. Roy. Soc.* A, **155,** 653.
KLAHR, C. N., 1951, *Phys. Rev.*, **82,** 109 ; **83,** 460.
KOHLER, M., 1941 a, *Z. Phys.*, **118,** 37 ; 1941 b, *Ibid.*, **118,** 312 ; 1941 c, *Ann. Phys., Lpz.*, (5), **40,** 601 ; 1949 a, b, c, *Ibid.*, (6), **5,** 89, 99, 181 ; 1949 d, *Ibid.*, (6), **6,** 18.
MAZUR, P., and PRIGOGINE, I., 1951, *J. Phys. Radium*, **12,** 616.
MEIXNER, J., 1939, *Ann. Phys., Lpz.*, (5), **35,** 701 ; 1941, *Ibid.*, (5), **40,** 165.
RIECKE, E., 1898, *Wied Ann.*, **66,** 545, 1199.
SHOCKLEY, W., 1950, *Electrons and Holes in Semiconductors* (New York : van Nostrand).
SOMMERFELD, A., and FRANK, N. H., 1931, *Rev. Mod. Phys.*, **3,** 1.
SONDHEIMER, E. H., 1948, *Proc. Roy. Soc.* A, **193,** 484 ; 1950 a, *Ibid.*, **203,** 75 ; 1950 b, *Phys. Rev.*, **80,** 401.
SONDHEIMER, E. H., and WILSON, A. H., 1947, *Proc. Roy. Soc.* A, **190,** 435.
TORREY, H. C., and WHITMER, C. A., 1948, *Crystal Rectifiers* (New York : McGraw-Hill).
WELKER, H., 1951, *Z. Naturforsch.*, **6,** 184.
WRIGHT, R. W., 1951, *Proc. Phys. Soc.* A, **64,** 984.

An Experimental Investigation of the Stability of Nuclei against Double Beta-Disintegration

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ABSTRACT. Samples containing elements of even Z have been examined for possible beta-activity using a photographic emulsion technique. For the elements Cr, Fe, Ni, Zn, Ge and Cd the results show that the effective half-value period for double beta-decay for the elements as a whole is in each case greater than 10^{17} years if the disintegration energy is 2 MEV or more (or greater than 10^{16} years if the disintegration energy is 0·35 MEV or more). For Ca, Mo, Sr, Sn, Te, Ba, W, Os and Pt lower limits between 2×10^{14} and 6×10^{16} years are similarly obtained on the assumption of 2 MEV disintegration energy, the residual uncertainty in most cases being due to the slight contamination of the samples with natural radio-elements. A possible weak beta-activity shown by samples containing Mo requires further examination.

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§ 1. INTRODUCTION

THE half-lives predicted for the process of double beta-decay depend strongly on the form of decay theory employed. On the basis of the Fermi theory the simultaneous emission of two electrons must be accompanied by the emission of two neutrinos. Transition probabilities for such a disintegration have been investigated by Goeppert-Mayer (1935), who showed that they are so low that the process is almost certainly unobservable directly, unless the decay energy is improbably high. Furry (1939) calculated the disintegration probabilities on the basis of the Majorana theory of beta-decay. In this case a double beta-disintegration could occur without the emission of neutrinos and with a correspondingly greater probability. The half-lives predicted in each of these cases for a nucleus for which $Z=31$, and for various values of the energy available, are quoted in table 1.

Table 1

Energy (MEV)		2	3	4	5	6	10
$T_{1/2}$ (years) :	Fermi	10^{25}	4×10^{22}	2×10^{21}	7×10^{19}	8×10^{18}	2×10^{16}
	Majorana	10^{15}	9×10^{13}	2×10^{13}	6×10^{12}	3×10^{12}	2×10^{11}

The experimental evidence available suggests that the probability of double beta-decay is considerably lower than that predicted by Majorana theory. Lower limits for the half-lives of ^{128}Te and ^{238}U of the order of 10^{19} years have been established by analysis for the reaction products (Inghram and Reynolds 1949, Levine, Ghiorso and Seaborg 1950), and an examination of palladium by Winter (1952) has established lower limits for the half-lives of the isotopes of even mass number of the order of 10^{18} years. A value for the half-life of ^{130}Te of $1{\cdot}4\times10^{21}$ years has also been determined by Inghram and Reynolds (1950) from an examination of the isotopic constitution of xenon from old tellurium ores.

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The activity reported by Fireman (1949) for ^{124}Sn, corresponding to a half-life for double beta-decay of $(6{\cdot}5 \pm 2) \times 10^{15}$ years, has not been confirmed by the recent work of Kalkstein and Libby (1952), who established a minimum half-life of 10^{17} years for this isotope. Fireman has also recently failed to confirm any activity (Fireman and Schwarzer 1952).

This paper reports an investigation of the possible activities of a number of elements of even atomic number from which minimum half-lives of the individual isotopes of the order of $10^{17}\,\eta$ years have been established, where η is the proportion of the isotope concerned in the natural element.

§ 2. THE DETECTION OF SMALL ACTIVITIES

The electron-sensitive photographic plate has been employed for the detection of these very low activities, since it permits continuous observation of the suspected materials over long periods of time. Since such plates record the passage of every ionizing particle which enters the emulsion layer, large numbers of tracks, due to cosmic radiation and general radioactive contamination, are formed even in the absence of a localized source. However, by shielding the plates within steel and lead screens at a depth of 1 860 ft. below ground, it has been found possible to reduce the background against which any activity must be observed from about 200 to 2·5 tracks per mm^2 of a 200 μ thick emulsion per day (Fremlin and Walters 1950). Also, with the co-operation of Messrs. Ilford Ltd. it has been possible to commence exposures with plates containing only some 50 tracks per mm^2 without using eradication processes. Such an initial track density is not a serious limitation when exposures of one or two months duration are made.

It was found convenient to expose thick sources of the substances examined to the surface of the plates rather than to incorporate them in the emulsion layer; this resulted in an increase in the ability to detect weak activities, since it is usually impossible to incorporate a large percentage of foreign material into the emulsion without loss of photographic sensitivity.

The technique employed was to embed a few grammes of high purity material into recesses in graphite blocks, powdered samples being bound with a few drops of a dilute solution of collodion in acetone, previous measurements having shown these substances to be inactive. The graphite blocks then faced the emulsion layer during the exposure. This exposure technique avoided chemical interaction by preventing actual contact between the sample and the emulsion, and also, by virtue of its simplicity, enabled a survey of a considerable number of elements to be made. Graphite was found convenient as a supporting material, since high purity samples could be obtained which showed no detectable activity and since it does not react chemically with the emulsion. The graphite used in these experiments was obtained from the Atomic Energy Research Establishment, Harwell. During the exposures the plates were stored in an atmosphere of nitrogen at a pressure slightly in excess of atmospheric, relative humidity being controlled by the presence of phosphorus pentoxide. Under such conditions exposures of four months' duration were made without latent-image fading or loss of photographic sensitivity.

After development the plates were examined independently by several observers and a count made of the electron tracks crossing the upper emulsion surface both in the regions exposed to the samples and in those which had faced the graphite. This resulted in a greater sensitivity for the detection of a pure β-emission than a count of all the tracks present throughout the emulsion layer; the existence of K-capture or γ-activity would not, however, be distinguished under these circumstances. Several exposures of different duration were made to each sample at intervals of a few months, so that the existence of any contamination by short-lived artificial radio-elements would be observed. All elements possessing stable isotopes isobaric with nuclei differing by two in atomic number were examined in this way, with the exception of some rare earth elements and the rare gases. The results of the activity measurements obtained in the longest exposure made to each sample are quoted below for all those materials which were obtainable in an uncontaminated condition. It was considered highly unlikely that any contamination by the long-lived natural beta-emitters could be significant. Contamination by uranium, thorium or their products, on the other hand, was probable but in all cases would be indicated by the appearance of α-particle tracks, and a count of these would enable an estimate to be made of the order of magnitude of the β-particle output to be expected from the contamination.

The activity of the graphite supports was examined in some detail and found to be of the order of 0·04 electron per mm² of its surface per day, which could, in general, be neglected in comparison with the statistical uncertainties involved in the measurement of the sample activities. Thus counts in regions of the plate exposed to graphite could be regarded as the background against which similar counts obtained in areas facing the samples should be compared. An investigation into the origin of the background tracks observed in plates exposed under these conditions has been made and will be described in a future publication.

§ 3. EXPERIMENTAL RESULTS

Table 2

Sample		Count in loaded area		Back-ground (β/mm²)	Exposure (days)	Sample activity (β/mm²/day)	Min. half-life $T_{1/2}/\eta$ (years)
		Electrons	α-particles				
CaCO$_3$	a	86·0±4·5	none	75·5±1·6	56	0·19±0·07	7×10^{16}
Chromium	a	66·0±4·0	4·3±0·6	66·0±3·0	27	0·00±0·15	$2{\cdot}2\times10^{17}$
Iron sponge	a	76·5±4·3	1·0±0·4	75·5±1·6	56	0·18±0·07	$1{\cdot}3\times10^{17}$
Nickel	b	52·0±1·6	0·5±0·1	52·5±1·6	27	0·00±0·07	$3{\cdot}2\times10^{17}$
Zinc	a	44·8±1·8	0·3±0·1	47·5±1·3	27	0·00±0·12	2×10^{17}
Germanium	a	50·0±1·7	none	52·5±1·6	27	0·00±0·08	$2{\cdot}8\times10^{17}$
Molybdenum	a	87·5±2·1	none	54·1±1·2	27	1·24±0·09	$1{\cdot}5\times10^{16}$
SrCO$_3$	a	79·1±3·4	none	63·8±1·5	56	0·27±0·07	$3{\cdot}4\times10^{16}$
Cadmium	99·99	86·0±4·6	4·5±1·0	75·5±1·6	56	0·19±0·09	10^{17}
SnO	a	94·0±4·8	1·5±0·5	63·8±1·5	56	0·56±0·09	$1{\cdot}4\times10^{16}$
^{124}Sn	*	138±7	20·6±1·4	46·4±2·3	15	6·1 ±0·5	2×10^{15}
Tellurium	a	77·5±5·0	none	63·8±1·5	56	0·24±0·11	$1{\cdot}3\times10^{16}$
BaCO$_3$	a	115±5	7±1	47·2±2·4	15	4·5 ±0·4	$1{\cdot}8\times10^{15}$
Tungsten	b	53·5±1·4	0·95±0·10	39·1±0·9	27	0·54±0·06	2×10^{16}
Osmium	a	311±20	51±10	75·5±1·6	56	40±3·6	$2{\cdot}3\times10^{14}$
Platinum	b	67·2±3·3	3·0±1·0	52·5±1·6	27	0·55±0·13	$1{\cdot}7\times10^{16}$

a: Johnson Matthey spectroscopically standardized; b: purity not known;
* separated isotope, A.E.R.E. Half-lives for $E=2$ MEV

Table 3 gives the expected disintegration energies for a few of the isotopes investigated, based both on the empirical mass tables drawn up by Metropolis and Reitwiesner (1950) and on experimental mass values where these are available.

Table 3

Isotope	% abundance	Isobars	% abundance	Energy difference between isobars (MEV) Theor.	Energy difference between isobars (MEV) Exp.
^{40}A.	99·57	^{40}Ca	96·92	−3·8	−0·3*
^{46}Ca	0·0032	^{46}Ti	7·95	1·3	
^{48}Ca	0·179	^{48}Ti	73·45	7·3	4·3*
^{58}Fe	0·33	^{58}Ni	67·76	−4·2	−1·35*
^{64}Ni	1·16	^{64}Zn	48·9	−0·9	−1·85*
^{120}Sn	33·03	^{120}Te	0·09	0·55	
^{122}Sn	4·78	^{122}Te	2·43	2·8	
^{124}Sn	6·11	^{124}Te	4·59	5·1	1·5 ± 0·4†
		^{124}Xe	0·094	−0·88	
^{126}Te	18·71	^{126}Xe	0·088	1·4	
^{128}Te	31·85	^{128}Xe	1·90	3·5	
^{130}Te	34·51	^{130}Xe	4·07	5·6	
		^{130}Ba	0·101	−0·06	

* Collins, Nier and Johnson (1951, 1952). † Hogg and Duckworth (1952).

§ 4. DISCUSSION OF MEASUREMENTS

The estimation of the minimum half-life which can be ascribed to any isotope as a result of these activity measurements involves the calculation of the specific activity of the sample corresponding to the observed activity at its surface. Libby (1947) has shown on empirical grounds that an activity equal to one-tenth of the total number of disintegrations occurring in a layer equal in thickness to the beta-particle range will be observed at the surface of a thick source for the case of a normal energy spectrum. The specific activity, and hence the minimum half-life ascribed to the element, therefore depends on the value assumed for the disintegration energy. The values quoted in table 2 correspond to a disintegration energy of 2·0 MEV. For any other assumed disintegration energy E the minimum half-life to be ascribed will be increased by a factor ϕ proportional to the β-particle range at energy E. Values of ϕ calculated from the range–energy relation given by Katz and Penfold (1952) are:

E (MEV)	0·25	0·5	1·0	1·5	2	3	4	5	10
ϕ	0·06	0·17	0·44	0·62	1	1·5	2·1	2·5	4·8

From this it can be seen that few of the minimum half-lives ascribed are likely to be in error by more than a factor of three or four for reasonable values of the energy available.

Considering now the detailed results given in table 2, it is clear that most of the elements examined show no evidence of any real activity. In several cases unmistakable β-activity was shown by the samples used, but the correlation between observed α- and β-activity is consistent with the assumption that practically all the activity is due to contamination by heavy radioactive elements. The only element for which clear evidence of activity exists is molybdenum and, even in this case, work on other samples with different chemical histories is desirable before the activity can be regarded as proved.

§5. CONCLUSION

The simplicity of the method used has made possible the examination of a considerably larger number of elements than could have been done by previous methods. In special cases, such as those in which inert gases are produced in the reaction, far weaker activities could be detected by the 'geological' method used by Inghram and Reynolds (1949). Where the inert gases themselves are suspected of activity, very high pressures would be required if the present method were to be employed, and the sensitivity would not be comparable with that available by using a well-screened counter-controlled cloud chamber for example. For most substances, however, the method appears capable of competing in sensitivity with other existing techniques.

Experimental values for the mass differences of the heavier pairs of isobars are greatly needed; it is believed, however, that the large number of elements which have been examined without yielding unmistakably positive activities has an appreciable cumulative value without these. At least a few pairs of isobars would be expected to possess sufficiently large mass differences to show marked activities if the no-neutrino hypothesis of double beta-decay were correct. Although, therefore, the minimum half-lives observable by the present method are not as large as those which have been recorded previously for one or two special cases, they represent useful evidence against this hypothesis in its simplest form.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor P. B. Moon for providing facilities for this investigation, and for his helpful suggestions and continued interest in the work.

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REFERENCES

COLLINS, T. L., NIER, A. O., and JOHNSON, W. H., JR., 1951, *Phys. Rev.*, **84,** 717; 1952, *Ibid.*, **86,** 408.
FIREMAN, E. L., 1949, *Phys. Rev.*, **75,** 323 (L).
FIREMAN, E. L., and SCHWARZER, D., 1952, *Phys. Rev.*, **86,** 451.
FREMLIN, J. H., and WALTERS, M. C., 1950, *Proc. Phys. Soc.* A, **63,** 1178 (L).
FURRY, W. H., 1939, *Phys. Rev.*, **56,** 1184.
GOEPPERT-MAYER, M., 1935, *Phys. Rev.*, **48,** 512.
HOGG, B. G., and DUCKWORTH, H. E., 1952, *Phys. Rev.*, **86,** 567.
INGHRAM, M. G., and REYNOLDS, J. H., 1949, *Phys. Rev.*, **76,** 1265 (L); 1950, *Ibid.*, **78,** 822 (L).
KALKSTEIN, M. I., and LIBBY, W. F. 1952, *Phys. Rev.*, **85,** 368 (L).
KATZ, L., and PENFOLD, A. S., 1952, *Rev. Mod. Phys.*, **24,** 28.
LEVINE, C. A., GHIORSO, A., and SEABORG, G. T., 1950, *Phys. Rev.*, **77,** 296 (L).
LIBBY, W. F., 1947, *Industr. Engng. Chem., Anal. Ed.*, **19,** 2.
METROPOLIS, N., and REITWIESNER, G., 1950, *Table of Atomic Masses*, N.P. 1980 (Oak Ridge, Tennessee: U.S. Atomic Energy Commission).
WINTER, R. G., 1952, *Phys. Rev.*, **85,** 687 (L).

The Theory of (d, t) Reactions

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ABSTRACT. Expressions for the angular distribution of tritons emitted from nuclei bombarded with deuterons have been obtained using Born's approximation and the non-perturbation method of Butler. Discussion of the effect of different forms of the triton wave function on the angular distribution is given. The theory is shown to explain the experimental angular distributions satisfactorily.

THE THEORY OF (d, t) REACTIONS

EXPERIMENTS on the emission of tritons from nuclei bombarded with deuterons reveal angular distributions similar to those observed in (d, p) and (d, d′) reactions. This leads one to expect that this reaction also is a direct process, proceeding from the initial to the final state without the formation of a compound nucleus. The mechanism proposed here is that of an inverse stripping reaction. One imagines a neutron attached to the initial nucleus to be drawn out and captured by the deuteron in its flight without the deuteron actually penetrating the nucleus.

There are two methods available for treating this type of reaction. One treatment is by Born's approximation, which has been used with success in the interpretation of experiments on (d, p) reactions (Bhatia *et al.* 1952), and the inelastic scattering of deuterons (Huby and Newns 1951). There is also a method which avoids the use of perturbation theory, and this has been used by Butler (1951) in his theory of the (d, p) reaction. Both these methods have been applied to the present problem.* Details of the calculation need not be given here since both methods have been published in full for the (d, p) reaction, and the modifications involved are straightforward.

The differential cross section can be written

$$\sigma(\theta) = |G(p)|^2 \sum_l A_l |M_l(k)|^2,$$

where the scattering angle appears in the quantities k and p which are given by $k^2 = ((M_f/M_i)k_d - k_t)^2 + 4(M_f/M_i)k_d k_t \sin^2\theta/2$, and $p^2 = (k_d/2 - k_t/3)^2 + \frac{2}{3}k_d k_t \sin^2\theta/2$, k_d and k_t being the wave numbers of the deuteron and triton given by $k_d = (2m_d E_d)^{1/2}/\hbar$ and $k_t = (2m_t E_t)^{1/2}/\hbar$, where m_d and m_t are the reduced masses of the deuteron and triton and E_d and E_t the energies of the deuteron and triton in the centre-of-mass system of coordinates; M_i and M_f are the masses of the initial and final nuclei respectively. The values of l, which is the angular momentum with which the neutron leaves the nucleus, are restricted by the selection rules $\mathbf{J}_f = \mathbf{J}_i + \mathbf{l} + \frac{1}{2}$, J_i and J_f being the spins of the initial and final nuclei respectively, and by the fact that l is even or odd according as the parities of the initial and final nuclei are the same or different. The A_l contain all factors

* I have not in fact used Butler's technique, but have followed a more elegant presentation of this non-perturbation method due to Dr. R. Huby, which involves the use of S-matrix theory.

not affecting the angular distribution. The factor $M_l(k)$ exhibits the maxima and minima which are characteristic of these reactions. This factor differs in the two methods of calculation and is, for Born's approximation,

$$M_l(k) = \left(\frac{\pi}{2ka}\right)^{1/2} J_{l+1/2}(ka), \qquad \ldots\ldots(1\,a)$$

and for the non-perturbation method,

$$M_l(k) = \kappa r_0 \left(\frac{\pi}{2kr_0}\right)^{1/2} J_{l+1/2}(kr_0) K_{l+3/2}(\kappa r_0) - kr_0 \left(\frac{\pi}{2kr_0}\right)^{1/2} J_{l+3/2}(kr_0) K_{l+1/2}(\kappa r_0), \qquad \ldots\ldots(1\,b)$$

κ being given by $\kappa = \{2m_n(\epsilon_t - Q - \epsilon_d)\}/\hbar$, ϵ_d and ϵ_t being the binding energies of the deuteron and triton, m_n the reduced mass of the neutron with respect to the final nucleus, and Q the Q-value of the reaction. The quantities a and r_0 are both lengths of the order of magnitude of a nuclear radius.

The factor $G(p)$ is the same in both the perturbation and non-perturbation treatments of the problem, and depends on the internal wave functions of the deuteron and triton. One would expect this factor to depend sensitively on the form of the internal wave function for the triton and particularly on the asymptotic form, since one requires essentially the probability that in a triton one particle is a considerable distance away from the other two. However, this is found not to be the case as the calculations given below show. It is also found that the deuteron wave function has little effect, which is to be expected. The factor $G(p)$ is calculated for three combinations of wave functions (we omit all multiplying constants).

(*a*) Using Irving's (1951) wave function for the triton, which has the correct asymptotic form, and an exponential wave function for the deuteron,

$$\chi_t = \exp\{-\beta(\Sigma R_{ij}^2)^{1/2}\}/(\Sigma R_{ij}^2)^n, \qquad \chi_d = \exp\{-\alpha R_{12}\}/R_{12},$$

we obtain

$$G(p) = \frac{1}{p}\int_0^1 \frac{\sin(4-2n)\phi}{(A^2+B^2)^{2-n}}\, x\, dx, \qquad \ldots\ldots(2\,a)$$

where $A = 1 + (\sqrt{2}\alpha/\sqrt{3}\beta)x$, $B = (\sqrt{2}p/\beta)(1-x^2)^{1/2}$, $\phi = \tan^{-1} B/A$. In calculations we take $\alpha = 0{\cdot}23 \times 10^{13}$ cm^{-1}, and Irving's values $n = \frac{1}{4}$ and $\beta = 0{\cdot}759 \times 10^{13}$ cm^{-1}, which give the correct binding energy for the triton.

(*b*) Using a gaussian wave function for the triton, and an exponential wave function for the deuteron,

$$\chi_t = \exp\{-\gamma^2 \Sigma R_{ij}^2\}, \qquad \chi_d = \exp\{-\alpha R_{12}\}/R_{12}.$$

(*c*) Using gaussian wave functions for both the deuteron and the triton,

$$\chi_t = \exp\{-\gamma^2 \Sigma R_{ij}^2\}, \qquad \chi_d = \exp\{-\alpha^2 R_{12}^2\},$$

we obtain

$$G(p) = \exp\{-p^2/2\gamma^2\}. \qquad \ldots\ldots(2\,(b)$$

In calculations we take $\gamma = 0{\cdot}25 \times 10^{13}$ cm since this gives the correct difference for the binding energies of ^{3}H and ^{3}He when the coulomb energy is taken into account (Bruno 1948). It also gives a triton of about the same size as Irving's wave function, as is seen if one calculates the mean distance and the mean square distance of one particle from the centre of mass of the triton. The cases (*b*) and (*c*) are interesting since the angular dependence is the same, and it shows that the deuteron wave function has very little effect on the angular distribution. A plot of $|G(p)|^2$ is shown in fig. 1 for case (*a*) and cases (*b*) and (*c*), and it is seen that the variation with p is very similar. Thus the form of the triton wave function also seems to have little effect. This increases confidence in the results obtained. It also makes the calculations easier since the gaussian wave functions give an answer in terms of elementary functions. For higher values of p, however, the difference between the results ($2a$) and ($2b$) becomes more marked, and in this region one would expect Irving's wave function to be the more satisfactory.

These results can be applied to the angular distribution of tritons emitted from the ^{9}Be(d, t)^{8}Be reaction. This has been measured by El-Bedewi (1951) and extended to lower scattering angles by Holt and Marsham.* The deuterons had energy 7·7 MEV in the laboratory system and the Q-value is 4·67 MEV. Figure 2 shows the experimental points together with curves drawn from the two theories ($1a$) and ($1b$) using $G(p)$ as given by ($2a$). The transition is $l=1$ and the values of the radii used are, in ($1a$), $a=6{\cdot}7\times10^{-13}$ cm, and in ($1b$), $r_0=5{\cdot}0\times10^{-13}$ cm. Using the selection rule, we find that if ^{9}Be has spin $\frac{3}{2}$ and odd parity, ^{8}Be has spin 0, 1, 2, 3 and even parity.

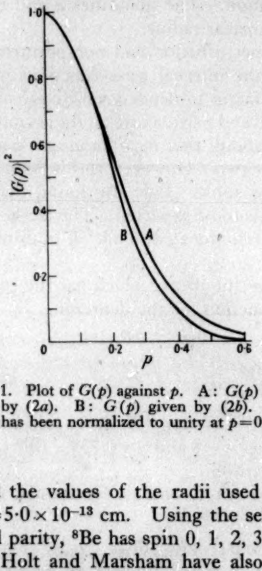

Fig. 1. Plot of $G(p)$ against p. A: $G(p)$ given by ($2a$). B: $G(p)$ given by ($2b$). $G(p)$ has been normalized to unity at $p=0$.

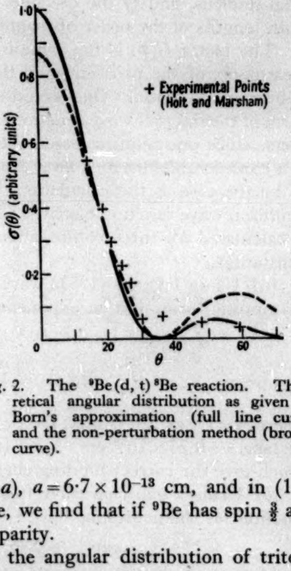

Fig. 2. The ^{9}Be(d, t)^{8}Be reaction. Theoretical angular distribution as given by Born's approximation (full line curve) and the non-perturbation method (broken curve).

Holt and Marsham have also measured the angular distribution of tritons from the ^{7}Li(d, t)^{6}Li reaction, and this is also consistent with an $l=1$ transition, which means that if ^{7}Li has spin $\frac{3}{2}$ and odd parity, ^{6}Li has spin 0, 1, 2, 3 and even parity. These results do not give any new information, but they are consistent with the usually accepted values of spin zero for ^{8}Be and spin 1 for ^{6}Li.

Comparison of the two methods is difficult since both seem to fit equally well. The Born approximation result has the advantage of greater ease of numerical calculation, but the non-perturbation method is possibly the better founded theoretically, and has a radius which seems to be remarkably stable at 5×10^{-13} cm. This latter method appears to fail in the (d, p) reaction, when the neutron enters the nucleus with energy so large that the final state is virtual.

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* I am indebted to Dr. J. R. Holt and Mr. T. N. Marsham for communicating their results before publication.

(A fuller discussion of this question of radii is given in Bhatia *et al.* 1952.) However, in this case this will not happen since the final nucleus in the (d, p) reaction corresponds to the initial nucleus in the present reaction, and one always starts with a stable nucleus.

Finally, Wolfgang and Libby (1952) have measured the total cross section of the ^{9}Be(d, t)^{8}Be reaction and have found it to be approximately constant at about 2×10^{-25} cm^2 over the range of energy from 3 to 8 Mev. It is difficult to estimate this theoretically, but a rough estimate can be made of 10^{-25} cm^2 at 8 Mev. In the limit of high energies the cross section varies as $1/E_{\mathrm{d}}$. These results are in as good agreement as can be expected with the experimental data.

In conclusion it may be pointed out that the above analysis will apply also to the (d, ^{3}He) reaction by changing all quantities relating to the triton to the corresponding ones for the ^{3}He nucleus. The parameters in Irving's wave function remain the same since these give the correct binding energy for the ^{3}He nucleus when the coulomb energy is taken into account.

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REFERENCES

Bhatia, A. B., Huang, K., Huby, R., and Newns, H. C., 1952, *Phil. Mag.*, **43**, 485.
Bruno, B., 1948, *Ark. Mat. Astr. Fys.* A, **36**, No. 8.
Butler, S. T., 1951, *Proc. Roy. Soc.* A, **208**, 559.
El-Bedewi, F. A., 1951, *Proc. Phys. Soc.* A, **64**, 947.
Huby, R., and Newns, H. C., 1951, *Phil. Mag.*, **42**, 1442.
Irving, J., 1951, *Phil. Mag.*, **42**, 338.
Wolfgang, R. L., and Libby, W. F., 1952, *Phys. Rev.*, **85**, 437.

Electron Capture
I: Resonance Capture from Hydrogen Atoms by Fast Protons

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ABSTRACT. Born's approximation is used to calculate the cross section associated with resonance charge exchange between protons and hydrogen atoms, it being pointed out that in earlier treatments of this problem unjustified simplifying assumptions were made. An energy range of up to 250 kev is covered. The predicted energy variation of the cross section is in harmony with the results of Ribe's recent laboratory work on collisions of protons with hydrogen molecules.

§ 1. INTRODUCTION

Electron capture through energetic collisions between positive ions and neutral atoms or molecules, besides being of interest in itself, is important in aurorae and in certain other natural phenomena. It is therefore desirable to carry out quantal calculations on the process. The simplest possible case

$$H^+ + H(1s) \rightarrow H(1s) + H^+ \qquad \ldots\ldots(1)$$

was studied many years ago by Oppenheimer (1928) and by Brinkmann and Kramers (1930) who gave a closed formula for the cross section which could readily be generalized to more complicated collisions. Unfortunately, examination of their treatment shows that the interaction potential employed is incorrect and that as a consequence so also are both the absolute magnitude and the energy variation of the deduced cross sections. The present paper is devoted to a reinvestigation of the problem. Attention will be restricted to the collision represented by (1), but the method is applicable to other cases and will be extended to them later.

§ 2. ANALYSIS

2.1

At high energies the cross section Q associated with the rearrangement collision

(nucleus A + electron e) + nucleus B → nucleus A + (nucleus B + electron e),

is given by Born's approximation (cf. Mott and Massey 1949) to be

$$Q = \frac{8\pi^3 M^2}{h^4}\frac{v_f}{v_i}\int_{-1}^{+1} |\mathcal{M}|^2\, d(\cos\theta) \qquad \ldots\ldots(2)$$

in which M is the reduced mass of the system, v_i and v_f are the magnitudes of the initial and final velocities of relative motion, θ is the angle between unit vectors $\mathbf{n}_i$ and $\mathbf{n}_f$ parallel to these velocities, and $\mathcal{M}$ is the relevant transition integral. Denoting the position vector of the centre of mass of (A + e) relative to B by $\boldsymbol{\rho}$, that of the centre of mass of (B + e) relative to A by $\boldsymbol{\sigma}$, and that of e relative to A and B by $\mathbf{r}$ and $\mathbf{s}$ respectively,

$$|\mathcal{M}| = \left|\iint \exp\left[i(k_i\mathbf{n}_i \cdot \boldsymbol{\rho} - k_f\mathbf{n}_f \cdot \boldsymbol{\sigma})\right]\phi_i(\mathbf{r})\phi_f^*(\mathbf{s})V(\mathbf{r},\mathbf{s})\, d\mathbf{s}\, d\boldsymbol{\sigma}\right| \qquad \ldots\ldots(3)$$

where

$$k_i = \frac{2\pi v_i}{h}\frac{(M_A + m)M_B}{M_A + M_B + m}, \quad k_f = \frac{2\pi v_f}{h}\frac{(M_B + m)M_A}{M_A + M_B + m}, \qquad \ldots\ldots(4)$$

ϕ_i is the initial and ϕ_f the final wave function of the electron, and $V(\mathbf{r},\mathbf{s})$ is the interaction potential between A and (B + e) which is

$$\frac{Z_A e^2}{r} - \frac{Z_A Z_B e^2}{|\mathbf{r} - \mathbf{s}|} \qquad \ldots\ldots(5)$$

$Z_A e$ and $Z_B e$ being the nuclear charges. Previous workers have taken only the first term of $V(\mathbf{r},\mathbf{s})$ into account, asserting that orthogonality would make the contribution from the second zero if proper wave functions were used. This simplification is without justification. In the standard collision theory treatment (cf. Mott and Massey 1949) the complete wave function $\Psi(\boldsymbol{\sigma},\mathbf{s})$ is expanded in the form

$$\sum_m F_m(\boldsymbol{\sigma})\phi_m(\mathbf{s}) \qquad \ldots\ldots(6)$$

and substituted in the Schrödinger equation yielding

$$(\nabla^2 + k_f^2)F_f(\boldsymbol{\sigma}) = \frac{8\pi^2 M}{h^2}\int \Psi(\boldsymbol{\sigma},\mathbf{s})V(\mathbf{r},\mathbf{s})\phi_f^*(\mathbf{s})\, d\mathbf{s} \qquad \ldots\ldots(7)$$

from which (2), with $\mathcal{M}$ defined as in (3), follows at once on making the usual approximation that

$$\Psi(\boldsymbol{\sigma},\mathbf{s}) \simeq \exp(ik_i\mathbf{n}_i \cdot \boldsymbol{\rho})\phi_i(\mathbf{r}). \qquad \ldots\ldots(8)\dagger$$

---

† In the case of identical nuclei, the wave function should, of course, be made antisymmetrical, but this is an unnecessary complication in an investigation concerned only with exchange scattering.

Clearly the contribution from the controversial term of $V(\mathbf{r},\mathbf{s})$ would *not* vanish even if, in place of (8), the exact expansion (6) were used. It would instead give on the right-hand side of (7) the function

$$\frac{8\pi^2 M}{h^2}\left\{-\frac{Z_A Z_B e^2}{|\mathbf{r}-\mathbf{s}|}\right\}F_f(\boldsymbol{\sigma}) \qquad \ldots\ldots(9)$$

which is certainly not negligible, being in fact equivalent to a coulomb potential on the left-hand side. The corresponding function resulting from the adoption of (8) is very different since the $\phi_f(\mathbf{s})$ content of $\exp(ik_i\mathbf{n}_i\cdot\boldsymbol{\rho})\phi_i(\mathbf{r})$ is far from equal to $F_f(\boldsymbol{\sigma})$. This is, to be sure, most grievous but it is not a reason for ignoring the $-Z_A Z_B e^2/|\mathbf{r}-\mathbf{s}|$ term of $V(\mathbf{r},\mathbf{s})$ altogether. The effect of $Z_A e^2/r$, the remaining term of $V(\mathbf{r},\mathbf{s})$, is also likely to be poorly represented. However, the similarity of the two terms suggests that the errors may partially cancel, especially if Z_A and Z_B are unity. In consequence approximation (8) may be not unsatisfactory. The situation is analogous to that arising in the more familiar case of excitation by electrons for which the interaction potential is of essentially the same form as that under discussion. Some early investigators thought that owing to orthogonality one of the two terms should be omitted. It is now known that such a procedure is incorrect and leads to serious overestimates of the exchange cross sections, particularly at low impact energies (cf. Bates, Fundaminsky, Leech and Massey 1950).

2.2

To evaluate $\mathcal{M}$ it is convenient (following Brinkmann and Kramers) to change the integration variables, and introduce the vectors

$$\boldsymbol{\alpha} = k_f\mathbf{n}_f + k_i\mathbf{n}_i M_A/(M_A+m) \qquad \ldots\ldots(10)$$

$$\boldsymbol{\beta} = -k_i\mathbf{n}_i - k_f\mathbf{n}_f M_B/(M_B+m) \qquad \ldots\ldots(11)$$

so that (3) may be written,

$$|\mathcal{M}| = \left|\iint \exp\,[i(\boldsymbol{\alpha}\cdot\mathbf{r}+\boldsymbol{\beta}\cdot\mathbf{s})]\phi_i(\mathbf{r})\phi_f^*(\mathbf{s})\left\{\frac{Z_A e^2}{r} - \frac{Z_A Z_B e^2}{|\mathbf{r}-\mathbf{s}|}\right\}d\mathbf{r}\,d\mathbf{s}\right|. \qquad \ldots\ldots(12)$$

If each of the nuclear changes is Z, and if ϕ_i and ϕ_f are 1s wave functions (12) becomes

$$|\mathcal{M}| = \left|\frac{Za^3e^2}{\pi}\iint \exp\,[i(\boldsymbol{\alpha}\cdot\mathbf{r}+\boldsymbol{\beta}\cdot\mathbf{s}) - a(r+s)]\left\{\frac{1}{r} - \frac{Z}{|\mathbf{r}-\mathbf{s}|}\right\}d\mathbf{r}\,d\mathbf{s}\right| \qquad \ldots\ldots(13)$$

where $a = Z/a_0$, a_0 being the radius of the lowest Bohr orbit of hydrogen. Moreover, it may easily be shown that K, the modulus of both $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, and δ, the angle between these two vectors, are given with sufficient accuracy by the simple equations

$$K^2 = \frac{2M^2p^2}{m^2a_0^{\,2}}(1+\cos\theta) + \frac{p^2}{4a_0^{\,2}}, \quad \cos\delta = \frac{p^2}{2K^2a_0^{\,2}} - 1 \qquad \ldots\ldots(14)$$

with $p = 2\pi m v a_0/h$, the subscript on v being omitted as unnecessary since the collision is elastic.

Integrals similar to (13) have been discussed by Massey and Mohr (1931) in connection with another problem. The contribution from the first term of the interaction potential may be obtained by elementary methods; that from the second term may be obtained by choosing the z-axis parallel to either $\boldsymbol{\alpha}$ or $\boldsymbol{\beta}$, expanding $1/|\mathbf{r}-\mathbf{s}|$ in the standard Legendre polynomial series, and using the formula

$$(-i)^n \int_{-1}^{+1} \exp(iz\mu) P_n(\mu)\, d\mu = (2\pi/z)^{1/2} J_{n+1/2}(z) = 2j_n(z) \qquad \ldots\ldots(15)$$

(cf. Watson 1944). Writing $t = K/a$ it is found that

$$|\mathscr{M}| = \left| \frac{4\pi Z e^2}{a^2} \left\{ f(t) - \sum_n (-1)^n P_n(\cos\delta) g_n(t) \right\} \right|, \qquad \ldots\ldots(16)$$

where $f(t) = 8/(1+t^2)^3$

$$g_n(t) = 4a^5 Z \int_0^\infty e^{-ar} j_n(Kr)$$
$$\times \left[r^{-(n-1)} \int_0^r e^{-as} s^{n+2} j_n(Ks)\, ds + r^{n+2} \int_r^\infty e^{-as} s^{-(n-1)} j_n(Ks)\, ds \right] dr$$
$$= 8a^5 Z \int_0^\infty e^{-ar} j_n(Kr) i_n(Kr) r^{(-n-1)}\, dr,$$

with $i_n(Kr) = \int_0^r e^{-as} s^{n+2} j_n(Ks)\, ds = -K^{n-1} \frac{\partial}{\partial K} \{K^{-(n-1)} i_{n-1}(Kr)\}$.

Simple analysis shows that

$$g_n(t) = \frac{Z}{t^2(1+t^2)^3} [A_n(t) - B_n(t) \log(1+t^2) - tC_n \tan^{-1} t],$$

$A_n(t)$ and $B_n(t)$ being polynomials and C_n being a constant. The first six members of the series (some of which have also been derived by Massey and Mohr) are as follows:

$A_0(t) = t^4 + 5t^2$
$B_0(t) = 0$
$C_0 \quad = 0$

$A_1(t) = 3t^4 + 21t^2 - 2$
$B_1(t) = 6t^2 - 12 - 2t^{-2}$
$C_1 \quad = 32$

$A_2(t) = 5t^4 + 85t^2 + 24 + 12t^{-2}$
$B_2(t) = 30t^2 + 0 + 30t^{-2} + 12t^{-4}$
$C_2 \quad = 96$

$A_3(t) = 7t^4 + 259t^2 + 438 + 498t^{-2} + 180t^{-4}$
$B_3(t) = 84t^2 + 252 + 672t^{-2} + 588t^{-4} + 180t^{-6}$
$C_3 \quad = 192$

$A_4(t) = 9t^4 + 615t^2 + 2500 + \frac{1}{3}(15710)t^{-2} + 4520t^{-4} + 1400t^{-6}$
$B_4(t) = 180t^2 + 1260 + 4800t^{-2} + 7380t^{-4} + 5220t^{-6} + 1400t^{-8}$
$C_4 \quad = 320$

$A_5(t) = 11t^4 + 1232t^2 + 9024 + 30245t^{-2} + 45840t^{-4} + 32550t^{-6} + 8820t^{-8}$
$B_5(t) = 330t^2 + 3960 + 21450t^{-2} + 50820t^{-4} + 61380t^{-6} + 36960t^{-8} + 8820t^{-10}$
$C_5 \quad = 480.$

Finally, substitution of (16) in (2) yields

$$Q(p^2) = \left[\frac{4}{p^2} \int_{p^2/4Z^2}^\infty \left| f(t) - \sum_n (-1)^n P_n\left(\frac{p^2}{2Z^2 t^2} - 1 \right) g_n(t) \right|^2 d(t^2) \right] \pi a_0^2. \qquad \ldots.(17)$$

The adoption of the infinite upper limit is justified by (14) which shows that when θ is zero K, and hence t, is extremely large. It may be noted that p^2, the variable in which Q is expressed, is m/M_A times the energy of relative motion of the incident nucleus measured in rydbergs; thus if the incident nucleus is a proton a p^2 of unity corresponds to an energy of $24{\cdot}9_7$ kev.

If the g_n terms are omitted the integration in (17) can be carried out analytically giving

$$Q(p^2) = \left[\frac{2^{18}Z^{10}}{5p^2}(p^2+4Z^2)^{-5}\right]\pi a_0^2, \qquad \text{......(18)}$$

which is, of course, identical with the formula obtained by Brinkmann and Kramers.

It is instructive also to consider the effect of ignoring the momentum transfer occurring when the electron is removed from the stationary to the incident nucleus. If m is neglected in (10) and (11) it can be seen that in this case the vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are antiparallel. Hence $P_n(\cos\delta)$ is $(-1)^n$, and the summation in the expression for Q can be replaced by

$$\sum_n g_n(t) = Z\left\{\frac{1}{(1+t^2)} + \frac{4}{3(1+t^2)^2} + \frac{8}{3(1+t^2)^3}\right\}, \qquad \text{......(19)}$$

as may be proved by the consideration of

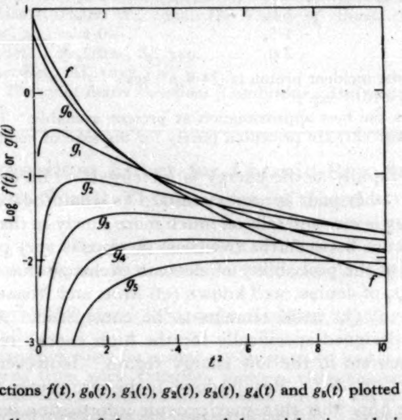
$$\iint \frac{1}{|\mathbf{r}-\mathbf{s}|}\exp\left[iK\mathbf{n}.(\mathbf{r}-\mathbf{s}) - a(r+s)\right] d\mathbf{r}\, d\mathbf{s}, \qquad \text{......(20)}$$

which can be evaluated easily (by, for example, using spheroidal coordinates). Since in addition the lower limit of the integral involved in it becomes zero, (17) thus reduces to $Q(p^2) = \{4/135p^2\}[1728 - 2592Z + 1067Z^2]\pi a_0^2$ or, if Z is unity, to

$$Q(p^2) = [6{\cdot}01/p^2]\pi a_0^2. \qquad \text{......(21)}$$

§ 3. RESULTS

The functions $f(t)$ and $g_n(t)$ ($n=0$ to 5, $t^2=0$ to 100) were computed from the expressions given in the previous section. Great cancellation occurs when t is small but fortunately a useful check on the work can be obtained from (19) since for such t the g_n series converges very rapidly. The figure shows the form of the functions in the earlier part of the range. A logarithmic scale is used. It will be noted that the g_n's decrease comparatively slowly, becoming much larger than f at quite moderate values of t^2, and further that one of them, g_0, is comparable with



Log of functions $f(t)$, $g_0(t)$, $g_1(t)$, $g_2(t)$, $g_3(t)$, $g_4(t)$ and $g_5(t)$ plotted against t^2.

f even at the origin. However, owing to the oscillatory character of the multiplying Legendre polynomials their influence on the magnitude of Q is not as great as might be supposed at first.

Formula (17) was evaluated by numerical methods with Z unity and with p^2 between 0 and 10 (which covers energies up to some 250 kev in the case of protons). Account was taken of only those members of the g_n series that are illustrated. The omission of the higher members probably makes the calculated cross sections slightly smaller or larger than they should be according to whether p^2 is below or above about 2, but from some calculations on the effect of including g_6 and g_7 (which were estimated by extrapolation) it seems most unlikely that an error of as much as 10% could be introduced.

The cross sections finally obtained from formula (17) are displayed in the table together with the corresponding cross sections obtained from formulae (18) and (21). For convenience, the formulae numbers will be used as identifying subscripts. It can be seen that Q_{18} is considerably greater than Q_{17} at low energies but falls off more rapidly as the energy is increased. The omission of the g_n's clearly provides a rather poor approximation. As would be expected Q_{21} equals Q_{17} when the energy is zero and falls off much more slowly so that at even moderate energies the difference between the two cross sections is very pronounced. The striking reduction of the probability of electron exchange due to the momentum transfer incurred is, of course, well known (cf. Mott and Massey 1949).

Cross Section associated with Resonance Charge Exchange between Protons and Hydrogen Atoms

Energy parameter* p^2	Log of cross section (in units of πa_0^2)†		
	formula (18)	formula (21)	formula (17)‡
(0·0)	$(1{\cdot}7_1 - \log p^2)$	$(0{\cdot}7_8 - \log p^2)$	$(0{\cdot}7_8 - \log p^2)$
0·4	$1{\cdot}9_0$	$1{\cdot}1_8$	$0{\cdot}9_8$
0·8	$1{\cdot}4_1$	$0{\cdot}8_8$	$0{\cdot}5_2$
1·2	$1{\cdot}0_6$	$0{\cdot}7_0$	$0{\cdot}2_0$
1·6	$0{\cdot}7_7$	$0{\cdot}5_8$	$-0{\cdot}0_6$
2·0	$0{\cdot}5_3$	$0{\cdot}4_8$	$-0{\cdot}2_8$
3·0	$0{\cdot}0_2$	$0{\cdot}3_0$	$-0{\cdot}7_4$
4·0	$-0{\cdot}4_0$	$0{\cdot}1_8$	$-1{\cdot}1_2$
5·0	$-0{\cdot}7_5$	$0{\cdot}0_8$	$-1{\cdot}4_4$
6·0	$-1{\cdot}0_6$	$0{\cdot}0_0$	$-1{\cdot}7_3$
8·0	$-1{\cdot}5_8$	$-0{\cdot}1_2$	$-2{\cdot}2_0$
10·0	$-2{\cdot}0_1$	$-0{\cdot}2_2$	$-2{\cdot}6_0$

* The energy of the incident proton is $(24{\cdot}9_7 p^2)$ kev.

† πa_0^2 equals $8{\cdot}8 \times 10^{-17}$ cm^2.

‡ Formula (17) is the best approximation at present available. The results obtained from formulae (18) and (21) are presented purely for the sake of comparison.

The reliability of Q_{17} itself remains to be considered. As the basic Born approximation is designed specifically for the high energy region it cannot be expected to be accurate in the low energy region. However, the range of its validity is not easy to predict. Results down to the zero energy limit are presented in the table in the hope that they may provide information on the matter when proper comparison data become available. At, and for some distance above, this limit, the cross sections given are certainly too large since in deriving them it was assumed that only transitions *into* the final state occur whereas *backward* transitions must be important. A theoretical investigation of this is in progress. The accuracy attained at moderate and high energies should be quite good though, as mentioned in § 2.1, assumption (8) is open to criticism in that what is relevant is not merely the general form, but a refined property, of the wave function (just as in the case of exchange excitation by electron impact, cf. Bates, Fundaminsky, Leech and Massey 1950).

No experiments have been carried out on proton–hydrogen atom collisions, but several workers have studied $H^+ + \mathrm{H}_2 \rightarrow \mathrm{H}' + \mathrm{H}_2^+$. Unlike (1) the process is not of the resonance type so the results obtained in the low energy region are of little significance in the present connection. The latest measurements in the moderate and high energy region are those of Ribe (1951). Over the range covered (for p^2 between about 1·5 and 6) the observed variation with energy is, within the stated experimental error, identical with that given by the theory. The absolute magnitudes of Ribe's cross sections (per hydrogen atom) are, however, about 1·5 times those predicted. Part of the discrepancy may be due to the fact that the measurements relate to the *total* exchange cross sections and thus include the contribution from capture into excited states. Some calculations on this contribution are planned. The cross sections may, of course, be influenced by the molecular binding but it would scarcely be anticipated that they are thereby increased.

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REFERENCES

Bates, D. R., Fundaminsky, A., Leech, J. W., and Massey, H. S. W., 1950, *Phil. Trans. Roy. Soc.* A, **243**, 93.
Brinkmann, H. C., and Kramers, H. A., 1930, *Proc. Acad. Sci., Amsterdam*, **33**, 973.
Massey, H. S. W., and Mohr, C. B. O., 1931, *Proc. Roy. Soc.* A, **132**, 605.
Mott, N. F., and Massey, H. S. W., 1949, *The Theory of Atomic Collisions* (Oxford : University Press) 2nd edn.
Oppenheimer, J. R., 1928, *Phys. Rev.*, **51**, 349.
Ribe, F. L., 1951, *Phys. Rev.*, **83**, 1217.
Watson, G. N., 1944, *Theory of Bessel Functions* (Cambridge : University Press), 2nd edn.

The Transition Effect for Cosmic-Ray Bursts at Small Thicknesses of Lead

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ABSTRACT. The transition curve for cosmic-ray bursts under lead at sea level is analysed to find the contributions from stars, extensive showers, electromagnetic interactions of μ-mesons, and single high-energy electrons and photons. When this is done, a substantial fraction of the bursts under lead thicknesses less than about 2·5 cm remains unaccounted for. It is suggested that they are produced by ' narrow air showers ' consisting predominantly of photons of about $2{\cdot}5 \times 10^8$ ev and having a sideways spread of less than 0·3 m.

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§ 1. INTRODUCTION

A feature of the transition effect for cosmic-ray bursts in an ionization chamber appears to have escaped notice until recently (Northrop 1951). This is an abrupt increase in the burst rate under small thicknesses of lead, tentatively attributed to narrow showers, i.e. air showers having a small lateral extension. In the absence of shielding, bursts can be produced by nuclear disintegrations (stars) and by extensive showers (Bridge *et al.* 1948, Carmichael 1948, Montgomery and Montgomery 1947, 1949). When the chamber is shielded, further burst-producing agencies become important. Bridge and Rossi (1949) account for the maximum of the transition curve at 10 000 ft in terms of bursts produced by single high-energy electrons and photons. At larger thicknesses bursts can be produced through electromagnetic interactions of μ-mesons (Christy and Kusaka 1941) or in nuclear interaction processes (Bridge and Rossi 1949, George and Trent 1951). It is the purpose of the present paper to point out that the above agencies are not sufficient to account for the transition effect of cosmic-ray bursts at small thicknesses of lead, and that some other agency must be presumed to be making a large contribution.

§ 2. APPARATUS

The apparatus consisted of complementary ion chamber and Geiger counter systems (Prescott and Mohr 1949, Campbell and Prescott 1952). The ion chamber was cylindrical, 57·6 cm long and 8·8 cm in diameter, filled to 39 atmospheres with nitrogen. Three Geiger counters in coincidence were located immediately above the chamber; these acted as a 'master group'. Counters located at 3 m and 5 m from the master group allowed bursts due to extensive showers to be identified. The efficiency of this arrangement for detecting extensive showers of the minimum density used in the analysis (600 particles/m^2, $4{\cdot}2 \times 10^5$ ion pairs) was 99%. The shielding consisted of hemicylindrical lead caps fitting over the chamber and extending one inch beyond the ends of the chamber and one inch below the centre on either side. Shielding thicknesses were 0·6, 1·2, 1·75, 2·3, 3·4 and 4·5 cm. The observations were carried out at sea level.

§ 3. RESULTS

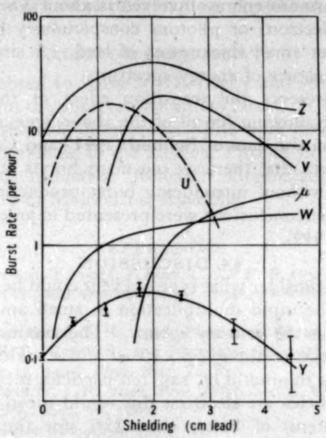
Burst-size distributions were obtained at all lead thicknesses and, from them, transition curves; these were essentially the same as similar results obtained by other authors (e.g. Young 1937, Schmid 1941, Carmichael 1948, Chou 1948). The burst-size distributions for zero, 0·6 and 1·2 cm of lead show the discontinuity of slope characteristic of distributions made up of more than one component (Carmichael 1948).

(*a*) A typical transition curve (for all bursts greater than $4{\cdot}2 \times 10^5$ ion pairs) is shown in the figure, curve Z. The statistical errors are within 1% for all points. Curve Y shows the transition effect for extensive showers as determined by the coincidence method described above.

(*b*) The rates of disintegration bursts arising in the walls of a shielded chamber can be found from the transition effect for stars in nuclear emulsions (Bernardini, Cortini and Manfredini 1949, 1950, George and Jason 1949, Schopper, Höcker and Kuhn 1951) and the observed rate in an unshielded chamber. These are equal to within a few per cent at all thicknesses of lead, since the transition effect is confined almost entirely to stars of three or four prongs which are relatively inefficient in producing bursts in the present chamber. The transition effect for wall disintegrations is shown as curve X.

(*c*) Fast protons from disintegrations (Harding 1951) in the lead shielding itself might produce bursts at larger thicknesses. The transition effect for this supplementary contribution was calculated and is shown in curve W.*

The main difficulty in constructing curve W is in determining the absolute rate. A straightforward calculation from the disintegration rates in lead gives only an order of magnitude ($\sim 0{\cdot}1$ per hour). An upper limit, which is all we shall require in the present case, can be found in the following way: Fahy (1951) finds that 68% of the bursts under 10·5 cm of lead at sea level are due to μ-mesons (knock-on and bremsstrahlung). Thus no more than 32% can be due to fast protons. Lapp (1946) gives the absolute rates of bursts of different burst sizes under thick lead shields. A burst of $4{\cdot}2 \times 10^5$ ion pairs in the present chamber is equivalent to a burst of 40 particles at minimum ionization, which gives, from Lapp's data, a rate of four per hour for bursts produced by μ-mesons and two per hour as an upper limit for those produced by fast protons. Curve W is extrapolated to two per hour at 10 cm. The true rate will actually be much less, since showers are also produced by nuclear collisions (George and Trent 1951, Fahy 1951). Indeed, Simpson, Baldwin and Uretz (1951) show that any increased contribution to the burst rate from stars in the lead is negligible under 2·5 cm of lead.



Analysis of the transition curve in lead for bursts greater than $4{\cdot}2 \times 10^5$ ion pairs

The transition curve for bursts produced by μ-mesons was very kindly calculated for the author by Mr. I. D. Campbell and is shown in curve μ, fitted as to absolute rate in the above manner. The important point about the curves W and μ is that their contribution is small for lead thicknesses less than about 2·5 cm.

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* This calculation is essentially the same as one outlined by Carmichael (1948). The energy spectrum of the fast protons which enters into the calculation was constructed from Harding's results (1951).

Fast protons from the atmosphere cannot produce bursts, since, under the prevailing conditions of gas pressure and bias, at least four such protons are required, even under the most favourable circumstances.

(*d*) We now consider the contribution of *single* high-energy electrons or photons. The minimum burst-size of $4{\cdot}2\times10^5$ ion pairs corresponds to 40 particles at minimum ionization. The transition effect is estimated by finding the relative numbers of electrons that are capable of producing 40 particles or more under each lead thickness (Bridge and Rossi 1949, Bhabha and Chakrabarty 1948). If we assume the integral energy spectrum of the initiating particles to be of the form E^{-s} (Rossi 1949), where s is taken to be 2, we obtain curve V. This curve includes the effect of fluctuations (assumed to be Poissonian), and the absolute rate is adjusted to account for as many bursts as possible. There appear to be no experimental observations at sea level with which this rate can be compared. The minimum energy involved is about 3×10^9 ev. It is seen that single high-energy electrons or photons conspicuously fail to account for the bursts observed under small thicknesses of lead. A similar result follows for any other reasonable choice of energy spectrum.

(*e*) Curve U represents the transition effect of the bursts that remain unaccounted for after allowing for all of the above agencies. A similar analysis roughly carried out on the data of Schmid (1941) and Chou (1948) leads to an identical conclusion, viz. that there are too many bursts at small lead thicknesses to be accounted for without introducing burst production by some additional agent. Similar general conclusions were presented in an earlier preliminary note (Prescott and Mohr 1949).

§ 4. DISCUSSION

It is of interest to consider what type of event could be invoked to account for the above result. The rapid multiplication in small amounts of lead requires electrons or photons as the primary agency. The maximum at about 1·2 cm of lead indicates an energy of about $2{\cdot}5\times10^8$ ev and a multiplication at maximum of 4·5. This means a minimum of, say, ten particles incident on the top of the shielding. If the particles are electrons this would mean an efficiency (from the geometry of the system) of better than 25% for the master group, i.e. a chamber–master group coincidence rate of about five per hour. The rate observed is only $0{\cdot}58\pm0{\cdot}07$ per hour, of which roughly half can be accounted for by extensive showers (Campbell and Prescott 1952).* This suggests that at least the greater part of the particles are photons which cannot discharge the counters. Support for this suggestion comes from evidence for the lateral spread of the showers.

The coincidence rate between two ionization chambers was observed at a separation of 0·32 m under shields of 0·6 and 1·2 cm of lead. No coincidences were recorded that could not be accounted for by extensive showers (Campbell and Prescott 1952), indicating that the sideways spread of the burst-producing showers is less than 0·32 m. Coincidences were also observed between the (unshielded) master group and counters at separations from 0·1 to 5 m. The coincidence rate did not increase significantly until the separation of the counters was less than 0·3 m, but then increased abruptly; this type of result with Geiger counters at lower densities is already well known (Wei and Montgomery 1949, Wei 1950, Alichanian and Asatiani 1945). The small spread for the shower particles shows either that they are produced very close above the apparatus or that, once produced, they are not scattered appreciably sideways. This would be the case if they consist mainly of photons as suggested above. The picture of the agency responsible for the large burst-rates under small thicknesses of lead consists, then, of a 'narrow shower' of photons of fairly low energy presumably accompanied by its parent particle and some slow electrons as well. If these 'narrow showers' are the same as those reported elsewhere (Wei and Montgomery 1949, Wei 1950) they also contain penetrating particles.

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* Of the balance, a burst can in isolated instances be identified as due to a narrow shower, e.g. very large bursts which fail to discharge another chamber only 0·32 m away, but the statistics are too poor to attempt to draw any detailed conclusions about, for instance, the proportion of ionizing particles present in the shower.

It does not appear possible without further experimental data to make any estimate of the absolute rate of narrow air showers without having to make arbitrary assumptions about the energy spectrum and number distribution of the particles in the shower and of their mode and point of origin.

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REFERENCES

Alichanian, A., and Asatiani, T., 1945, *J. Phys. U.S.S.R.*, **9**, 175.
Bernardini, G., Cortini, G., and Manfredini, A., 1949, *Phys. Rev.*, **76**, 1792; 1950, *Ibid.*, **79**, 952.
Bhabha, H. J., and Chakrabarty, S. K., 1948, *Phys. Rev.*, **74**, 1352.
Bridge, H. S., Hazen, W. E., Rossi, B., and Williams, R., 1948, *Phys. Rev.*, **74**, 1083.
Bridge, H. S., and Rossi, B., 1949, *Phys. Rev.*, **75**, 810.
Campbell, I. D., and Prescott, J. R., 1952, *Proc. Phys. Soc.* A, **65**, 258.
Carmichael, H., 1948, *Phys. Rev.*, **74**, 1667.
Chou, C. N., 1948, *Phys. Rev.*, **74**, 1659.
Christy, R. F., and Kusaka, S., 1941, *Phys. Rev.*, **59**, 414.
Fahy, E. F., 1951, *Phys. Rev.*, **83**, 413.
George, E. P., and Jason, A. C., 1949, *Proc. Phys. Soc.* A, **62**, 243.
George, E. P., and Trent, P. J., 1951, *Proc. Phys. Soc.* A, **64**, 733.
Harding, J. B., 1951, *Phil. Mag.*, **42**, 63.
Lapp, R. E., 1946, *Phys. Rev.*, **69**, 321.
Montgomery, C. G., and Montgomery, D. D., 1947, *Phys. Rev.*, **72**, 131; 1949, *Ibid.*, **76**, 1482.
Northrop, J. A., 1951, *Phys. Rev.*, **84**, 83.
Prescott, J. R., and Mohr, C. B. O., 1949, *Austral. J. Sci. Res.* A, **2**, 184.
Rossi, B., 1949, *Rev. Mod. Phys.*, **21**, 104.
Schmid, H., 1941, *Z. Phys.*, **117**, 452.
Schopper, E., Höcker, K. H., and Kuhn, G., 1951, *Phys. Rev.*, **82**, 444.
Simpson, J. A., Baldwin, H. W., and Uretz, R. B., 1951, *Phys. Rev.*, **84**, 332.
Wei, J., 1950, *Phys. Rev.*, **79**, 670.
Wei, J., and Montgomery, C. G., 1949, *Phys. Rev.*, **76**, 1488.
Young, R. T., 1937, *Phys. Rev.*, **52**, 559.

On a Modified Definition of Riesz Potential for the Meson Case

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ABSTRACT. A modified definition of the Riesz potential for the meson field is introduced. It is shown that the new definition is a generalization, in the α-plane, of the meson potential in the interaction representation. The relations satisfied by the meson potential in the interaction and in the Schrödinger representations are compared.

§ 1. INTRODUCTION

In a recent paper Auluck and Kothari (1951) have introduced a modified definition for the Riesz potential for the electromagnetic field, and Kothari and Bhatnagar (1952) have shown that the new definition is a generalization of the Wentzel potential* in the α-plane, α being an arbitrary parameter characteristic of the Riesz potential. The purpose of the present note is to extend the modified definition for the Riesz potential to the case of neutral vector mesons. The extension seems to be of interest, as the new potential is a generalization of the meson potential in the interaction representation. The definition of Fremberg (1946) for the meson case, on the other hand, reduces to meson potential in the Schrödinger representation when analytically continued to $\alpha = 0$. The equations satisfied by the meson potentials in the two representations are compared.

§ 2.

We define the metric tensor $g_{\mu\nu}$ as $g_{00}=1$; $g_{11}=g_{22}=g_{33}=-1$; $g_{\mu\nu}=0$ $(\mu \neq \nu)$. The velocity of light is taken as unity. The scalar product of two four-vectors A_μ, B_μ is denoted by $[AB]$:

$$[AB]=A_\mu B^\mu = A_0B_0 - A_1B_1 - A_2B_2 - A_3B_3 = A_0B_0 - (AB),$$

where (AB) is the three-dimensional scalar product of the space parts of A_μ and B_μ. The (positive) length of the space part of A_μ is denoted by $|A|$.

For the neutral vector meson case we define the Riesz potential $A_\mu{}^\alpha(x)$ at any point x as

$$A_\mu{}^\alpha(x) = H(\alpha)\int_{\mathrm{D}} (k^2-\chi^2)^{(\alpha-2)/2}\{A_{k\mu}\,e^{i[kx]} + \bar{A}_{k\mu}e^{-i[kx]}\}d^4k, \qquad \ldots\ldots(1)$$

where $H(\alpha)=2/\Gamma(\frac{1}{2}\alpha)\Gamma(1-\frac{1}{2}\alpha)=(2/\pi)\sin\frac{1}{2}\pi\alpha$, $k^2=[kk]$, and χ is the rest mass of the meson. The domain of integration D is the region defined by $k^2 \geqslant \chi^2$, $k_0>0$, k being the momentum four-vector of the meson. The above integral is convergent for $\alpha>0$. The coefficients $A_{k\mu}$ are so far arbitrary. It is easily verified that $A_\mu{}^\alpha(x)$ satisfies the equation

$$(\Box - \chi^2)A_\mu{}^\alpha(x) = A_\mu{}^{\alpha+2}(x). \qquad \ldots\ldots(2)$$

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* It may be noted here that the Wentzel potential (Dirac 1947) and the potential for the electromagnetic field in the interaction representation are the same.

Taking $f_\mu(z)$ to represent the most general interaction between the meson and the nucleon field, we write

$$A_{k\mu} = \frac{1}{4\pi^2 i}\int_S f_\mu(z)\, e^{-i[kz]}\, d^4z, \qquad \ldots\ldots(3)$$

where the integral is taken throughout the space S given by $z_0 \leqslant x_0$. Substituting this in (1), we have

$$A_\mu^\alpha(x) = \frac{H(\alpha)}{2\pi^2}\int_D\int_S (k^2-\chi^2)^{(\alpha-2)/2} f_\mu(z) \sin[k, x-z]\, d^4k d^4z. \qquad \ldots\ldots(4)$$

It is readily shown that $A_\mu^{\alpha+2}(x)$, as defined by (4), vanishes when analytically continued to $\alpha=0$. Combining this result with (2) and putting $A_\mu^0(x) \equiv A_\mu(x)$ we have

$$(\Box - \chi^2)A_\mu(x) = 0. \qquad \ldots\ldots(5)$$

Further,

$$\frac{\partial A_\mu^\alpha}{\partial x_\mu} = \frac{H(\alpha)}{2\pi^2}\int_D\int_S (k^2-\chi^2)^{(\alpha-2)/2} f_\mu(z) k^\mu \cos[k, x-z]\, d^4k d^4z. \qquad \ldots(6)$$

The right-hand side, in general, does not vanish when analytically continued to $\alpha=0$. Thus eqns. (5) and (6) show that the Riesz potential defined by (4) (or by (1) and (3)) is a generalization in the α-plane of the 'meson potential in the interaction representation'. In the limit $\alpha \to 0$ the new definition reduces to ordinary meson potential in interaction representation.

It is difficult to evaluate the right-hand side of (6) as α tends to zero in the general case. Physically also we are more interested in the interaction of a point particle with the meson field. We therefore proceed to evaluate (6) for this particular case.

For a point particle of mesic charge g moving along a world line $z = z(\tau)$, τ being its proper time, the coefficients $A_{k\mu}$ become

$$A_{k\mu} = \frac{1}{4\pi^2 i}\int_{-\infty}^{z} v_\mu'\, e^{-i[kz']}\, d\tau'. \qquad \ldots\ldots(7)$$

It follows from this that

$$k^\mu A_{k\mu} = \frac{g}{4\pi^2} e^{-i[kz]}, \quad k^\mu \bar{A}_{k\mu} = \frac{g}{4\pi^2} e^{i[kz]}. \qquad \ldots\ldots(8)$$

Hence we obtain from (1)

$$\begin{aligned}\frac{\partial A_\mu^\alpha(x)}{\partial x_\mu} &= -\frac{gH(\alpha)}{2\pi^2}\int_D (k^2-\chi^2)^{(\alpha-2)/2} \sin[k, x-z]\, d^4k,\\ &= -g\mathscr{D}_\chi^\alpha(x-z), \qquad \ldots\ldots(9)\end{aligned}$$

where

$$\mathscr{D}_\chi^\alpha(x) \equiv \frac{H(\alpha)}{2\pi^2}\int_D (k^2-\chi^2)^{(\alpha-2)/2} \sin[kx]\, d^4k. \qquad \ldots\ldots(10)$$

Now consider the integral

$$I^\alpha(x) = \int_D (k^2-\chi^2)^{(\alpha-2)/2}\, e^{i[kx]}\, d^4k.$$

Changing the variables of integration from k_0, k_1, k_2, k_3 to k, k_1, k_2, k_3, where $k^2 = k_0^2 - |k|^2$ (the Jacobian for the transformation is $k(k^2+|k|^2)^{-1/2}$), we have

$$I^\alpha(x) = \int_\chi^\infty (k^2-\chi^2)^{(\alpha-2)/2}\, k\, dk \int \frac{\exp\{ix_0(k^2+|k|^2)^{1/2} - i(kx)\}}{(k^2+|k^2|)^{1/2}}\, d^3k.$$

To integrate over d^3k we introduce polar coordinates, with the polar axis parallel to the vector (k_1, k_2, k_3). Integration over the angles can now easily be carried out, giving

$$I^\alpha(x) = \frac{2\pi}{i|x|}\int_\chi^\infty (k^2-\chi^2)^{(\alpha-2)/2} k\,dk \int_0^\infty \frac{|k|\,d|k|}{(k^2+|k|^2)^{1/2}} e^{ix_0(k^2+|k|^2)^{1/2}}\{e^{i|x||k|} - e^{-i|x||k|}\},$$

$$= -\frac{2\pi}{|x|}\int_\chi^\infty (k^2-\chi^2)^{(\alpha-2)/2} k\,dk \frac{\partial}{\partial|x|}\int_{-\infty}^\infty \frac{\exp\{ix_0(k^2+a^2)^{1/2} + ia|x|\}}{(k^2+a^2)^{1/2}}\,da. \qquad \ldots\ldots(11)$$

The integral over a can be evaluated in terms of Bessel functions:

$$\int_{-\infty}^\infty \frac{\exp\{ix_0(k^2+a^2)^{1/2}+ia|x|\}}{(k^2+a^2)^{1/2}}\,da = \begin{cases} i\pi H_0^{(1)}(ks) & \text{for } x_0 > |x| \\ i\pi H_0^{(1)}(ks) & \text{for } |x| > x_0 > -|x| \\ -i\pi H_0^{(2)}(ks) & \text{for } -|x| > x_0 \end{cases} \qquad \ldots\ldots(12)$$

where $k = (k^2)^{1/2}$ and $s = (x_0{}^2 - |x|^2)^{1/2}$.
Substituting back from (12) and (11) in (10) we get

$$\mathscr{D}_\chi{}^\alpha(x) = H(\alpha)\int_\chi^\infty (k^2-\chi^2)^{(\alpha-2)/2} k \frac{1}{|x|}\frac{\partial}{\partial|x|} U(ks)\,dk, \qquad \ldots\ldots(13)$$

where
$$-U(ks) = \begin{Bmatrix} J_0(ks) & \text{for } x_0 > |x| \\ 0 & \text{for } |x| > x_0 > -|x| \\ -J_0(ks) & \text{for } -|x| > x_0. \end{Bmatrix} \qquad \ldots\ldots(14)$$

The expression for $\mathscr{D}_\chi{}^\alpha(x)$ is clearly singular on the light cone $x_0 = |x|$. The nature of the singularity on the light cone is of the form

$$\Delta(x) = \frac{1}{|x|}\{\delta(x_0 - |x|) - \delta(x_0 + |x|)\} = \frac{2x_0}{|x|}\delta[xx].$$

Thus we have

$$\mathscr{D}_\chi{}^\alpha(x) = H(\alpha)\int_\chi^\infty (k^2-\chi^2)^{(\alpha-2)/2} k \left\{\frac{1}{|x|}\frac{\partial}{\partial|x|} U + \Delta(x)\right\} dk.$$

To continue the above expression to $\alpha = 0$ we introduce a new variable t, defined as $t^2 = k^2 - \chi^2$. In terms of this

$$\mathscr{D}_\chi{}^\alpha(x) = H(\alpha)\int_0^\infty t^{\alpha-1}\left\{\frac{1}{|x|}\frac{\partial}{\partial|x|} U\{s(t^2+\chi^2)^{1/2}\} + \Delta(x)\right\} dt, \qquad \ldots\ldots(15)$$

and hence

$$\mathscr{D}_\chi{}^0(x) = \Delta(x) + \frac{1}{|x|}\frac{\partial}{\partial|x|} U(\chi s)$$

$$= \Delta(x) - \frac{1}{s}\frac{\partial}{\partial s} U(\chi s). \qquad \ldots\ldots(16)$$

It will be noticed that the function $\mathscr{D}_\chi{}^0(x)$ is the same as the D-function for a particle of mass χ, used by Dirac (1934), Schwinger (1948) (Schwinger's Δ) and others.

The meson potential in the interaction representation thus satisfies the equations

$$(\Box - \chi^2)A_\mu(x) = 0, \quad \partial A_\mu(x)/\partial x_\mu = -g\mathscr{D}_\chi{}^0(x-z). \qquad \ldots\ldots(17)$$

These may be compared with the equations satisfied by meson potential in Schrödinger representation:

$$(\Box - \chi^2)\mathscr{A}_\mu(x) = gv_\mu, \quad \partial\mathscr{A}_\mu(x)/\partial x_\mu = 0. \qquad \ldots\ldots(18)$$

In the absence of nucleons the two sets of equations are the same. When nucleons are present it is the second equation that gets modified for the potential in interaction representation, while for the potential in the Schrödinger representation it is the first equation that is altered. It may also be noted that by putting $\chi=0$ in (17) we pass over to the Wentzel potential (Dirac 1947).

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REFERENCES

Auluck, F. C., and Kothari, L. S., 1951, *Proc. Camb. Phil. Soc.*, **47**, 436.
Dirac, P. A. M., 1934, *Proc. Camb. Phil. Soc.*, **30**, 150; 1947, *Quantum Mechanics* (Oxford : University Press), §78.
Fremberg, N. F., 1946, *Proc. Roy. Soc.* A, **188**, 18.
Kothari, L. S., and Bhatnagar, P. L., 1952, *Proc. Nat. Inst. Sci., India*, in the press.
Schwinger, J., 1948, *Phys. Rev.*, **74**, 1439.

Alkyl Shifts in Absorption Spectra of Azulene and other Aromatic Molecules

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ABSTRACT. An inquiry is made into the factors which cause shifts in the ultra-violet spectra of aromatic molecules on substitution. The method of molecular orbitals is used, and the discussion is confined to π-electrons. It is shown that there are two chief effects : the first is essentially electrostatic, or inductive ; the second is essentially conjugative, or mesomeric. In alternant hydrocarbons the second predominates and causes a red shift. In other molecules (e.g. azulene, quinoline) the first effect is considerably larger and now predominates over the second. Different positions of substitution will lead to shifts, sometimes to the red and sometimes to the blue. Electron donors will cause shifts in opposite directions to electron acceptors. The importance of these variations in characterizing the electronic transitions is stressed. Detailed investigation of the various methyl azulenes confirms the assignment of the long wavelength band with almost complete certainty.

§ 1. INTRODUCTION

It is a well-known fact that in normal aromatic molecules alkyl replacement of one of the boundary hydrogen atoms causes a shift of the long-wave ultra-violet spectrum to the red. In azulene, however (Plattner 1941 and later papers), certain positions of the methyl substitution shift the band to the red, other positions shift it to the blue. And in heteronuclear molecules, as Brown (1952) has recently pointed out, the shifts vary considerably with position of substitution, and are often larger than the shifts with normal aromatics. (A 'normal' hydrocarbon is here defined as one with no odd-numbered rings: more precisely it is an alternant hydrocarbon, in the language of Coulson and

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Longuet-Higgins (1947 a).) Ever since Mulliken's (1939) first account this alkyl shift has been interpreted as due to hyperconjugation. Yet, despite this, the phenomenon itself has by no means been satisfactorily explained; nor does its significance appear to have been fully recognized as a diagnostic tool whereby we can identify and classify electronic transitions in conjugated molecules. It is the object of this paper to give a fuller account than hitherto of the effect of alkyl and other substitution on the characteristic ultra-violet absorption of the parent compound. The questions to which we shall attempt to provide an answer are the following:

(i) Why are normal alkyl shifts to the red?

(ii) What factors determine the variation in shift of frequency with position of substitution?

(iii) What factors determine the absolute magnitude of the shift, and why are these shifts usually larger for non-alternant hydrocarbons and heteronuclear aromatics than for normal hydrocarbons?

(iv) Why are these shifts for molecules other than normal hydrocarbons sometimes to the red, and sometimes to the blue, and why do different substituents (e.g. —CH_3 and —COOH) often lead to shifts in opposite directions?

(v) How may an experimental determination of the directions and relative magnitudes of the shifts with different positions of substitution be used to characterize the type of electronic transition involved?

We shall see that reasonably convincing answers can now be provided to all these questions. Essentially our argument rests on a distinction between two aspects of the total effect of substitution. We have called these the electrostatic effect and the delocalization effect. By this we do not mean that they can be entirely separated from each other, for they cannot. But the ideas behind our rough separation correspond to pictures which have been visualized by chemists for some time, and their combination certainly provides a model which accounts for all the main features (i)–(v) above.

§ 2. THE MODEL

Since the transitions with which we are concerned take place in the region associated with π-electrons, we deal directly only with these. Any σ-electron effects which may exist are translated into terms applicable to π-electrons. As is usual in dealing with ultra-violet spectra, we find it more convenient to use the molecular-orbital (m.o.) description of the π-electron orbitals. In this each π-electron is described by a wave function which is a linear combination of $2p\pi$ atomic orbitals (a.o.) on the separate atoms. As far as possible we use the notation of Coulson and Longuet-Higgins (1947 a). Thus, any m.o. in the unsubstituted molecule is of the form

$$\psi = c_1\phi_1 + \ldots. + c_n\phi_n = \Sigma c_r\phi_r, \text{ say.} \qquad \ldots\ldots(1)$$

The energy ϵ associated with this orbital is defined in terms of the coefficients c_r, together with the Coulomb term α_r of each atom and the resonance integral β_{rs} of each bond. α_r measures the electronegativity of the atom (i.e. the attraction of the atom for π-electrons), and β_{rs} measures the strength of a double bond between atoms r and s (i.e. the attraction of the bond for π-electrons). We suppose that each α_r and β_{rs} is known. If necessary, as shown by Wheland and Mann (1949), by Altmann (1950) and by Chirgwin (unpublished), we may have to determine the α_r and β_{rs} by some sort of iterative procedure. In what follows we regard them all as known. Then the coefficients c_r for each separate m.o. ψ are found from the normal secular equations. We suppose that these also are available. They can, of course, be calculated separately for the substituted molecules also, as was done by Pullman, Mayot and Berthier (1950), but this, though it provides a numerical value for the displacement of the band, does not enable us to understand how these displacements arise, or to answer the questions (i)–(v) of the introduction.

In the simple form of the m.o. theory which we are using we calculate the allowed energy levels and then allot the electrons to these levels, generally filling the lowest levels first. Each allocation of electrons gives rise to what we may call a configuration. We make the assumption that each such configuration by itself is a good approximation to a real state of the molecule. This means that we neglect all configuration interaction of the kind discussed by Coulson, Craig and Jacobs (1951). It seems most unlikely that such configuration interaction would materially affect the small energy shifts on substitution with which we are here concerned. In a similar way we neglect all σ–π resonance of the type recently discussed by Altmann (1952). It would not be very easy to include this in a m.o. treatment, except through the inclusion of considerable configuration interaction, and its inclusion here does not appear to be necessary in order to understand our phenomenon and calculate approximate values for the various shifts. In any complete treatment, however, it would be necessary to incorporate it.

If we accept the foregoing assumptions, then the frequency of any band (strictly the $0-0$ frequency, since we do not consider the vibrational pattern of the bands) is given very simply by the difference in energy of the two molecular orbitals, corresponding to an electron jump from ψ_1 to ψ_2:

$$h\nu = \Delta E = \epsilon_2 - \epsilon_1. \qquad \ldots\ldots(2)$$

In what follows we shall need the formula for the energy of the m.o. ψ. It is

$$\epsilon = \frac{c_1{}^2\alpha_1 + c_2{}^2\alpha_2 + \ldots. + 2c_1c_2\beta_{12} + \ldots.}{1 + 2c_1c_2S_{12} + \ldots.}. \qquad \ldots\ldots(3)$$

This formula follows immediately from the energy relation

$$\epsilon = \int \psi H \psi \, d\tau \Big/ \int \psi^2 \, d\tau,$$

where H is the effective Hamiltonian for a single π-electron. We use the standard definitions of α_r and β_{rs}:

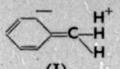
$$\alpha_r = \int \phi_r H \phi_r \, d\tau, \qquad \beta_{rs} = \int \phi_r H \phi_s \, d\tau,$$

and suppose that the overlap integrals S_{rs} are defined by $S_{rs} = \int \phi_r \phi_s \, d\tau = S_{sr}$, $S_{rr} = 1$. When we wish to distinguish the coefficients c_r for the two orbitals ψ_1 and ψ_2 we shall write them c_{r1} and c_{r2} respectively. The normalization in (3) is such that $c_1{}^2 + c_2{}^2 + \ldots. = 1$.

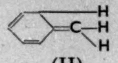
§ 3. THE TWO EFFECTS OF SUBSTITUTION

Consider a methyl substituent. We know from the reactivity of toluene and from dipole moments, etc. (cf. Cohn, Hughes, Jones and Peeling 1952) that when it is substituted in an aromatic molecule the methyl group acts as an electron donor. We also know that it is able to conjugate with the aromatic nucleus of the original molecule. These two effects together comprise what we call hyperconjugation. Since, however, this is a single phenomenon, we have no genuine right to distinguish the two partial components just listed. But, as stated earlier, it is interesting to do so, and helps us to understand the phenomena associated with substitution (cf. Matsen 1950).

The electron donor effect is sometimes represented, in resonance theory, by structures such as (I), and the conjugation, or electromeric, effect by structures such as (II). In m.o. language (I) is very similar to an electrostatic influence exerted on the aromatic nucleus, and could be called either the 'electrostatic effect' or the 'inductive effect', since it is induced in the original unsubstituted molecule by the presence of the substituent. The effect represented by (II) is much less dependent on this electronegative character: it is essentially an additional delocalization of the π-electrons of the unsubstituted molecule. It would exist even if the substituent were a vinyl group, where the electrostatic effect would be much reduced. For that reason we shall refer to these two aspects of substitution as the electrostatic effect and the delocalization effect. As we shall see, their influences on the spectral properties of the molecule are quite distinct. And, by means of the distinction, we are able to provide intelligible and semi-quantitative answers to the original questions (i)–(v).



(I)



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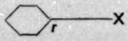
§4. THE ELECTROSTATIC EFFECT



We suppose that the substituting group X is attached at position r of the conjugated molecule. The electrostatic effect arises from the fact that the bond C_r—X is polar, so that electrons are either pushed towards C_r (electron donor) or away from C_r (electron acceptor). In either case we can say that there will be a small change in the effective electronegativity of atom r. Since, at this stage, it is chiefly σ-electrons that are being displaced, this effect is essentially the inductive effect of Cohn *et al.* (1952). Now the electronegativity of atom r is measured by the Coulomb term α_r. So with electron donors such as —CH_3 we shall have $\delta\alpha_r > 0$, and with electron acceptors such as —COOH we shall have $\delta\alpha_r < 0$. This change in α_r will affect all the π-electron m.o.'s and alter their energies. According to (3) the alteration in energy will be

$$\delta\epsilon = \left(\frac{\partial\epsilon}{\partial\alpha_r}\right)\delta\alpha_r = (c_r^2/N)\,\delta\alpha_r, \qquad \ldots\ldots(4)$$

where N is written for $1+2\Sigma c_1 c_2 S_{12}$, and we have supposed that $\delta\alpha_r$ is sufficiently small for first-order perturbation theory to be applicable. We shall return to this condition later.

It follows from (4) that

$$\delta(\epsilon_2-\epsilon_1) = \left\{\frac{c_{r2}^2}{N_2} - \frac{c_{r1}^2}{N_1}\right\}\delta\alpha_r. \qquad \ldots\ldots(5)$$

Now for the top occupied and lowest unoccupied orbitals in most conjugated systems $2\Sigma c_1 c_2 S_{12}$ is fairly small, of the order of $\frac{1}{8}$. It is therefore a reasonable approximation to put $N_2 = N_1 = 1$. Equation (5) then shows that

$$\delta(h\nu) = (c_{r2}^2 - c_{r1}^2)\times\delta\alpha_r. \qquad \ldots\ldots(6)$$

This result allows us to make two important deductions:

(*a*) Since $\delta(\boldsymbol{h}\nu)$ is proportional to $\delta\alpha_r$, we should expect that the effect of substitution will change from bathochromic to hypsochromic, or vice versa, if we change the sign of $\delta\alpha_r$. This gives us an immediate explanation of point (iv) in the introduction. For, as Plattner and colleagues (1948, 1951) have shown experimentally, carboxylic substitution affects the long wavelength band of azulene in the opposite direction to methyl substitution. This is exactly what would have been expected if the displacement represented by (6) dominated the phenomenon.

(*b*) With the same substituent, but with different positions of substitution, we shall expect $\delta(\boldsymbol{h}\nu)$ to vary as $(c_{r2}^2 - c_{r1}^2)$. Now a simple consideration of these coefficients in the ground and excited states shows that this expression will be positive for certain *r*, and negative for others. Thus a single substituent should sometimes cause hypsochromic and sometimes bathochromic shifts, in complete accordance with the experimental results summarized by Brown (1952).

This completes our answer to point (iv), but it does not deal with one very important situation. This is the case of alternant hydrocarbons. For here, as Coulson and Rushbrooke (1940) have shown (see also Coulson 1948), the longest wavelength allowed transition is associated with molecular orbitals ψ_2 and ψ_1 where, in (1), we have

$$c_{r1} = \pm c_{r2} \qquad \ldots\ldots(7)$$

$$\Sigma c_{r1}c_{s1} = -\Sigma c_{r2}c_{s2}, \qquad \ldots\ldots(8)$$

and the summation is taken over all neighbours *rs*. If we call this sum A, then $A > 0$, and is usually of the order of magnitude of $\frac{1}{4}$. If we insert (7) in (6) we get a zero result. This means that we are no longer at liberty to neglect the overlap integral S in (5). Using (7) and (8) in (5), and supposing that S has the same numerical value (approximately $\frac{1}{4}$) for all neighbouring atoms, and that $S = 0$ for all non-neighbours, we may write

$$\delta(\boldsymbol{h}\nu) = \frac{2AS}{1 - A^2S^2} c_{r1}^2 \delta\alpha_r.$$

This is effectively

$$\delta(\boldsymbol{h}\nu) = 2ASc_r^2 \times \delta\alpha_r. \qquad \ldots\ldots(9)$$

We are to use (9) rather than (6) when dealing with alternant hydrocarbons. But this immediately answers some of the other questions (i)–(v). For

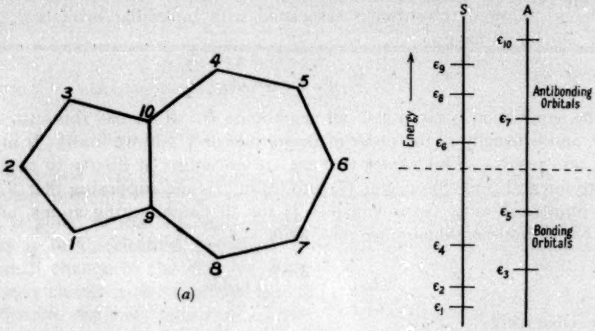
(*c*) The shifts are smaller than before. This is because $2AS$ is of order $\frac{1}{8}$; we should therefore anticipate shifts of the order of a quarter (or less) of the previous magnitudes. In this way we deal with the second part of question (iii).

(*d*) The shifts associated with the same substituent, but at different positions *r*, are now all of the same sign. For methyl substitution, where $\delta\alpha_r > 0$, we should expect $\delta(\boldsymbol{h}\nu) > 0$, leading to a hypsochromic shift. This is the opposite of what is actually found, and it shows us that the delocalization effect must be considered as well as the electrostatic effect. Since we have seen in (*c*) that these latter are smaller in alternant hydrocarbons than in other aromatics, it is not surprising that delocalization effects should be relatively more important in the former than the latter.

(*e*) In comparing a heteronuclear molecule such as quinoline with its corresponding alternant hydrocarbon, here naphthalene, we should expect corresponding bands in the heteronuclear molecule to be shifted to the red as compared with the hydrocarbon. This is because $\delta\alpha_r$ is negative for a nitrogen atom relative to a carbon. Shifts of this kind are frequently observed. Our analysis, however, deals only with $\pi \rightarrow \pi^*$ transitions, and says nothing about possible transitions of a non-bonding nitrogen σ-electron to an anti-bonding π-orbital. Recent analysis suggests that these may play an important part in the complete spectrum of the heteromolecule. They do not exist in the hydrocarbon.

§ 5. METHYL AZULENES

Before concluding this discussion of the electrostatic (or inductive) effect we should like to show how powerful a tool it is in the characterization of these electronic transitions. This is a very complex problem, and so far very few really definite conclusions have been drawn for polynuclear molecules other than benzene. It will be convenient to illustrate our argument by specific reference to the methyl azulenes, for which excellent data are available. Pullman, Mayot and Berthier (1950) have already shown that the directions of the methyl displacements in the five distinct positions of substitution are in accord with theory. But these authors do not appear to have realized how remarkably clear-cut the argument is, and how definitely it characterizes the transition itself.



(a)

Fig. 1.

(b)

Let us assume, then, that in the methyl azulenes the electrostatic effect is more important than the conjugation, or delocalization, effect. In view of our earlier comments and the work of Cohn *et al.* (1952) this seems quite probable. What we can now do is to discuss the detailed changes that are induced in the energies of the molecular orbitals as a result of the change $\delta\alpha_r$. Figure 1 shows the numbering system for the molecule. We have also shown, in two columns, the energies of the orbitals for the unsubstituted compound. These are numbered in ascending order and fall into two groups, here called S and A for short, according as the m.o'.s themselves are symmetrical or antisymmetrical with respect to reflection in a plane perpendicular to the molecule and passing through its axis of symmetry 2–6. The actual coefficients c_r have been calculated by several authors (e.g. Coulson and Longuet-Higgins 1947 b, Wheland and Mann

1949), using simple assumptions about the constancy of resonance integrals and Coulomb terms. In the present work, however, new values due to B. H. Chirgwin have been used. These include allowance for uneven distribution of charge on the various nuclei, and for differences in β_{rs} and S_{rs} due to unequal bond lengths. The writer is grateful to Mr. Chirgwin for providing these in advance of publication.

If we refer to these m.o.'s in terms of their energies, there would appear to be five states of the molecule, comprising the ground state G and four excited states A–D, which might be expected to be significant in the visible and ultraviolet region. These are shown below, together with (1) the type of transition assuming that absorption takes place from the ground state, (2) the direction of polarization, which must be either parallel or perpendicular to the symmetry axis, and (3) the nomenclature proposed by Mann, Platt and Klevens (1949, referred to as MPK) in their comparison of the observed spectra of azulene and naphthalene. These transitions are listed in increasing sequence of energy,

	Occupied orbitals	Transition	Polarization	MPK designation
G	$\epsilon_1^2\ \epsilon_2^2\ \epsilon_3^2\ \epsilon_4^2\ \epsilon_5^2$			
A	$\epsilon_1^2\ \epsilon_2^2\ \epsilon_3^2\ \epsilon_4^2\ \epsilon_5\ \epsilon_6$	$\epsilon_5 \to \epsilon_6$	$\perp$	L_b
B	$\epsilon_1^2\ \epsilon_2^2\ \epsilon_3^2\ \epsilon_4\ \epsilon_5^2\ \epsilon_6$	$\epsilon_4 \to \epsilon_6$	$\parallel$	L_a
C	$\epsilon_1^2\ \epsilon_2^2\ \epsilon_3^2\ \epsilon_4^2\ \epsilon_5\ \epsilon_7$	$\epsilon_5 \to \epsilon_7$	$\parallel$	B_b
D	$\epsilon_1^2\ \epsilon_2^2\ \epsilon_3\ \epsilon_4^2\ \epsilon_5^2$	$\epsilon_3 \to \epsilon_6$	$\perp$	K_b

and were identified by MPK with four transitions actually occurring in the absorption spectrum in this order. This identification is plausible and agrees reasonably well with the energy differences calculated. But, as a growing body of evidence for naphthalene is beginning to show, great caution is needed in interpreting transitions in conjugated molecules in any simple manner. What we are now going to show is that the effects of methyl substitution allow an almost unequivocal decision to be reached concerning the long wave transition. Table 1 shows the values of $c_{r2}^2 - c_{r1}^2$ for the four possible transitions. An italic figure in this table corresponds to a hypsochromic shift on methylation at that position.

Table 1. Values of $c_{r2}^2 - c_{r1}^2$

Band	Atom $r=$ 1	2	4	5	6
A	−0·28	*0·10*	*0·19*	−0·11	*0·25*
B	−0·05	−0·21	*0·16*	−0·01	*0·11*
C	−0·18	0	*0·09*	*0·11*	0
D	−0·05	*0·10*	−0·02	−0·11	*0·25*

Now the positions of hypsochromic shift with the long wave band of azulene are precisely 2, 4 and 6. This, as Pullman and colleagues showed, agreed excellently with the interpretation of this band as being A. But now we see that there is no other possibility. It is only if this band is really due to a transition of type $\epsilon_5 \to \epsilon_6$ among the allowed molecular orbitals that even the correct signs are obtained for the shifts. It is true that we have here neglected the conjugative effect. But we shall show shortly that this effect can only shift energy bands to the red: no hypsochromic shifts are possible by this means. Hence only band A can be the visible band. In addition to this, we have evidence that the conjugative effect is of smaller magnitude than the inductive effect, since it is not able to change the figures in the table by as much as 0·1. This discussion deals partly with point (v) at the beginning. But the agreement is really quite surprisingly good from another aspect—the relative methyl shifts at different positions. Absolute values cannot be estimated since we do not know the magnitude of $\delta\alpha_r$; but if we choose $\delta\alpha_r$ so that the shift at position 1 agrees with experiment, then we get table 2. At the bottom of the table are shown Pullman's calculations.

Table 2

Position	1	2	4	5	6
$\Delta\lambda$ expt. (mμ)	41	−21	−17	18	−16
$\Delta\lambda$ calc. C.A.C.	[41]	−15	−26	16	−37
$\Delta\lambda$ calc. Pullman	[41]	−6	−6	20	−13

It is clear that not only are the directions of the shifts correct, but so also, to good accuracy, are the magnitudes. The shift at position 1 is the largest, in agreement with experiment. By no conceivable process could an agreement even remotely as good as this be obtained by any other interpretation of the long wave band.

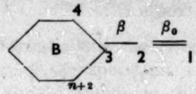
This is also in agreement with COOH substitution. In position 5 the shift is -15. This is less than $+18$ and of opposite sign. The opposite sign arises from the change of sign in $\delta\alpha_r$, and the smaller value is consistent with a small conjugating (delocalization) effect in opposition to the inductive effect in COOH substitution, but not in —CH_3 substitution. Also, in position 6, the —COOH shift is $+63$. This is of the expected sign, and should be larger than 16, since now inductive and conjugative effects cooperate. But it is somewhat larger than we should have expected, showing that the situation is really a little more complicated than our simple analysis suggests. Despite this, however, there seems little doubt but that the displacements due to methylation have served to identify the transition with a degree of certainty greater than that for any other polynuclear molecule hitherto studied.

A slightly unexplained feature is that in all the methyl substitutions of the next two bands (now in the ultra-violet and not the visible region) the shifts are always to long waves. We should have expected that some might have been to shorter waves. They are also much less numerically, except that a phenyl group, where the inductive effect can only be small, conjugates freely and gives a large (40 mμ) shift. Since a methyl must obviously conjugate much less than a phenyl this confirms that normally—i.e. except in odd-numbered rings—the conjugative effect is of the same order of magnitude as the inductive, but in odd-numbered rings it will often be of a smaller order of magnitude.

§ 6. THE CONJUGATION (i.e. DELOCALIZATION) EFFECT

All that remains is to discuss the conjugation effect, and to show that in all normal circumstances it leads to a red-shift. A discussion of resonance energy and bond length along these lines has already been given by Mulliken, Rieke and Brown (1941). But as we are interested only in spectroscopic properties we are able both to simplify the analysis and make it more generally applicable.

In order to avoid all mention of electrostatic or inductive effects we must suppose that the substituent is of equal or similar electronegativity to the carbon atom where it is attached. The simplest assumption is that instead of —$C{\equiv}H_3$ we have a vinyl group, —$CH{=}CH_2$. A similar analysis can be given for other non-polar substituents. Let us therefore discuss a system such as that in the diagram where B stands for any aromatic residue, not necessarily benzene. It will be convenient to number the carbon atoms as shown, and to suppose that the resonance integrals are β and β_0:



Let us suppose that the m.o.'s for B are known and have the form

$$\psi_j = \Sigma_r c_{rj}\phi_r, \qquad r=3, 4, \ldots\ n+2, \qquad j=3, 4, \ldots\ n+2$$

with energies $\epsilon = \epsilon_j$ (measured relative to a carbon π-orbital energy as zero). What we want to study is the way in which the ϵ_j are changed when the vinyl group is substituted at atom 3. To do this we express the m.o.'s for the total system as linear combinations of ϕ_1 and ϕ_2, which are the atomic orbitals of the vinyl carbons, and the ψ_j, which are m.o.'s for B alone. It will be recognized that this way of setting up the secular equations is a mixture of the usual method, where we employ only a.o.'s, and the LCMO method recently developed by Dewar (1949), where we employ only m.o.'s. The secular determinant is

$$\Delta \equiv \left| \begin{array}{cc|cccc} -\epsilon & \beta_0 & & 0 & & \\ \beta_0 & -\epsilon & c_{33}\beta & c_{34}\beta & \cdots & c_{3,n+2}\beta \\ \hline & c_{33}\beta & \epsilon_3-\epsilon & & & \\ & c_{34}\beta & & \epsilon_4-\epsilon & & \\ & \vdots & & & \ddots & \\ 0 & \vdots & & & & \\ & c_{3,n+2}\beta & & & & \epsilon_{n+2}-\epsilon \end{array} \right| = 0.$$

In this section, for convenience, we have neglected all overlap integrals. In the lower right-hand $n \times n$ section only the leading diagonal terms of Δ are non-vanishing. Expansion of this determinant gives

$$\Delta = (\epsilon^2 - \beta_0^2)\Pi(\epsilon_j - \epsilon) + \epsilon\beta^2\Pi(\epsilon_j - \epsilon)\sum_j \frac{c_{3j}^2}{\epsilon_j - \epsilon}.$$

So the new energies are the roots of the equation

$$(\epsilon^2 - \beta_0^2) + \epsilon\beta^2\Sigma \frac{c_{3j}^2}{\epsilon_j - \epsilon} = 0. \qquad \ldots\ldots(10)$$

The only circumstances in which this is invalid are those in which, for symmetry reasons, one or more of the levels of B are unaffected by substitution. We exclude this. It can be dealt with simply, if necessary, when it arises.

Solutions of (10) are most simply regarded as given by the intersections of the two curves

$$y = \epsilon\beta^2\Sigma \frac{c_{3j}^2}{\epsilon_j - \epsilon}, \qquad y = -(\epsilon^2 - \beta_0^2). \qquad \ldots\ldots(11)$$

There are $n+2$ roots, as we should expect from a system containing $n+2$ atoms in the conjugating framework. Figure 2 illustrates the intersection of these curves for the particular case of $n=4$. It can be verified from this—and is easily proved directly from (10)—that the following relationships hold between the original roots ϵ_j and the new roots ϵ_j':

$$\left.\begin{array}{llll} \text{if} & \epsilon_j > -\beta_0, & \text{then} & \epsilon_j' > \epsilon_j \\ & |\epsilon_j| < -\beta_0, & & |\epsilon_j'| < |\epsilon_j| \\ & \epsilon_j < \beta_0, & & \epsilon_j' < \epsilon_j. \end{array}\right\} \qquad \ldots\ldots(12)$$

In addition to the roots (12) there are the 'vinyl roots' $\pm\beta_0$. These may be shifted either upward or downward, but the shifts will not be expected to be large.

Now in the ground state of these molecules all the levels for which $\epsilon<0$ are doubly occupied, all the others being empty. Thus in the unsubstituted B of fig. 2 the lowest transition is of the type $\epsilon_4 \rightarrow \epsilon_5$. Quite clearly, since the result of vinyl substitution is to shift both ϵ_4 and ϵ_5 closer towards $\epsilon=0$, the energy difference $\epsilon_5'-\epsilon_4'$ is less than $\epsilon_5-\epsilon_4$. This argument will hold for all these molecules provided only that $|\epsilon_4|$ and $|\epsilon_5|$ are less than β_0. This is satisfied in all cases of interest. It follows that the delocalization effect is always in the direction of a shift to long waves. This is the basic explanation of point (i) in the introduction. We can also see that this conclusion is unaffected if, for symmetry reasons, referred to above, one of the levels ϵ_4, ϵ_5 is unchanged: for the other level will be changed, and in such a direction as to cause a bathochromic shift.

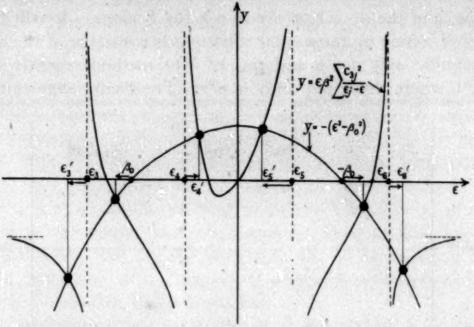


Fig. 2. Curves to illustrate the displacement of term values due to vinyl-substitution. The arrows along the axis of ϵ denote the energy displacements.

There is a simple pictorial description of the phenomenon we have just been describing. We could think of the vinyl substitution as a conjugation of B and $—CH=CH_2$. If we place the orbital energies ϵ_j of the original molecule B and the energies $\pm\beta_0$ of the vinyl group on the same diagram the resulting energies can be thought of as derived from these unperturbed energies by supposing that levels from different 'parts' repel each other. It will be recognized that the rule (12) is merely a transcription of this.

Both experience and calculation show that the delocalization shifts are not large. We may therefore solve eqn. (10) by approximate methods. These show that, to first order,

$$\epsilon_j' = \epsilon_j + \frac{\epsilon_j \beta^2 c_{3j}^2}{(\epsilon_j^2 - \beta_0^2) + \epsilon_j \beta^2 \sum\limits_{i \neq j} c_{3i}^2/(\epsilon_i - \epsilon_j)}. \qquad \ldots\ldots(13)$$

A rough verification of this formula may be obtained, as follows: Since, for transitions in the same region of the spectrum, $\epsilon_j \beta^2$ will not vary by a factor greater than about 2 : 1, we should anticipate that a strong correlation should exist between $\epsilon_j' - \epsilon_j$ and c_{3j}^2. Now if there are n carbon atoms in the unsubstituted molecule BH, the normalization condition shows that c_{3j}^2 is of order $1/n$. So we should expect that with alternant hydrocarbons the delocalization shift of frequency should vary approximately as $1/n$. Individual c^2 values may differ considerably from the value $1/n$, and so, where possible, we should consider the mean alkylation shift, when the methyl group is substituted, in turn, at all positions in the molecule. This we have done for a series of molecules, with the results shown in table 3. It is quite extraordinary that although the number of atoms in the molecule and the mean $\Delta\nu$ change by a factor of nine or more, the total spread of $n\Delta\nu$ values is less than 30% from the mean. This somewhat unexpected result provides confirmation of the general description of these alkylation shifts that we have been investigating. We must, however, be careful not to conclude from table 3 that the conjugation effect necessarily far outweighs the inductive effect. The fact, as represented by eqns. (9) and (13), seems to be that both effects have a magnitude which depends on c_r^2. It is this situation which is confirmed by the values calculated in the table.

Table 3

Molecule	n	Approximate region of spectrum (Å)	Mean $\Delta\nu$ (cm^{-1})	$n\Delta\nu$	Comments
Ethylene	2	2000	3800	7600	(1)
Benzene	6	2600	1100	6600	
Naphthalene	10	2800	530	5300	(2)
Anthracene	14	3800	500	7000	(3)
Benzanthracene	18	3600	320	5800	(4)
			250	4500	(5)

(1) Comparison of ethylene and propylene ; (2) data in American Petroleum Institute Research Programme 44, serial numbers 88, 89, 130–2, ultra-violet absorption spectrograms ; (3) see Jones 1945; bands labelled F, G, H. ; (4) long wave band H ; (5) average of bands F, G, H, I in data of Jones 1940, and of Badger, Pearce and Pettit 1952.

§ 7. CONCLUSION

Our conclusions are best put in the form of answers to the five questions which were posed in § 1. They are:

(i) Normal alkyl shifts in the long wavelength band are to the red as a result of greater delocalization of the π-electrons; this effect is more important than the electrostatic, or inductive, effect for alternant hydrocarbons.

(ii) The variation in frequency shift with position of substitution depends essentially on the square of the coefficient (c_r^2) in the LCAO molecular orbital for the top occupied level.

(iii) In alternant hydrocarbons the delocalization effect appears to be larger than the electrostatic effect: and in fact this latter by itself would give rise to blue shifts. But in other molecules, including both non-alternant hydrocarbons such as azulene, and heteronuclear molecules such as quinoline, the electrostatic effect is shown to be several times larger than before, and dominates the phenomenon.

(iv) In non-alternant hydrocarbons and heteromolecules the electrostatic effect depends on the product of an induced change of coulomb term $\delta\alpha_r$ at the position of substitution, and the difference $(c_{r2}^2 - c_{r1}^2)$ of the squares of the LCAO coefficients in the two orbitals involved. The variation with $\delta\alpha_r$ shows that the electron-donating groups (e.g. methyl) and electron-accepting groups (e.g. carboxyl) should give shifts in opposite directions. The variation with $c_{r2}^2 - c_{r1}^2$ shows that even with one substituent the shifts will be in different directions with different positions of substitution.

(v) A careful study of the predicted directions and relative magnitudes of the shifts due to methylation at all possible positions on the perimeter of the molecule can sometimes be used to characterize the electronic transition in an unambiguous way. A detailed analysis of the methyl azulenes gives a clear verification of the interpretation of the long wave band put forward by Mann, Platt and Klevens on other grounds.

Almost all of the above is in accord with experiment. There are a few exceptions, not properly understood, and there seem to be difficulties in applying these arguments to other than the longest wavelength allowed transitions. But certain new features have been suggested, notably the variation of the mean shift for all possible positions in a given molecule with the increase of the number of carbon atoms. This applies, naturally enough, only to alternant hydrocarbons.

One final comment needs to be made. We have where necessary assumed that first-order perturbation theory could be used. This is equivalent to the assumption that the shifts due to two or more substituents are additive. This appears quite satisfactory for alternants. Thus the successive shifts in the series benzene → toluene → p-xylene are 78 Å and 75 Å respectively. In the methyl azulenes a slightly less strict additivity obtains; but it is certainly good enough for our purposes provided that we exclude—as obviously we must—cases of steric interference.

Note added later

Since this paper was communicated a paper has appeared by Longuet-Higgins and Sowden (1952) in which part of the theory given here has been discussed from a somewhat different point of view. The same distinction is made between the inductive and conjugative effects, but in discussing the inductive effect the overlap integral is omitted so that the replacement of eqn. (6) by eqn. (9) for alternant hydrocarbons does not occur. Instead it is assumed that the inductive effect is actually zero. However, we have shown that the first-order effect with methyl substitution is necessarily hypsochromic. A further difference occurs with the hyperconjugative effect, where our argument is quite general, and that of Longuet-Higgins and Sowden is based on second-order perturbation theory. It is gratifying that in so far as the two accounts overlap they lead to similar conclusions.

REFERENCES

Altmann, S. L., 1950, *Proc. Phys. Soc.* A, **63**, 1234 ; 1952, *Proc. Roy. Soc.* A, **210**, 327, 343.
Badger, G. M., **Pearce**, R. S., and **Pettit**, R., 1952, *J. Chem. Soc.*, 1112.
Brown, R. D., 1952, *Nature, Lond.*, **169**, 287.
Cohn, H., **Hughes**, E. D., **Jones**, M. H., and **Peeling**, M. G., 1952, *Nature, Lond.*, **169**, 291.
Coulson, C. A., 1948, *Proc. Phys. Soc.*, **60**, 257.
Coulson, C. A., **Craig**, D. P., and **Jacobs**, J., 1951, *Proc. Roy. Soc.* A, **206**, 297.
Coulson, C. A., and **Longuet-Higgins**, H. C., 1947 a, *Proc. Roy. Soc.* A, **192**, 16 ; 1947 b, *Rev. Sci., Paris*, **15**, 929.
Coulson, C. A., and **Rushbrooke**, G. S., 1940, *Proc. Camb. Phil. Soc.*, **36**, 193.
Dewar, M. J. S., 1949, *Proc. Camb. Phil. Soc.*, **45**, 638.
Jones, N., 1940, *J. Amer. Chem. Soc.*, **62**, 148 ; 1945, *Ibid.*, **67**, 2127.
Longuet-Higgins, H. C., and **Sowden**, R. G., 1952, *J. Chem. Soc.*, 1404.
Mann, D. E., **Platt**, J. R., and **Klevens**, H. B., 1949, *J. Chem. Phys.*, **17**, 481.
Matsen, F. A., 1950, *J. Amer. Chem. Soc.*, **72**, 5243.
Mulliken, R. S., 1939, *J. Chem. Phys.*, **3**, 375.
Mulliken, R. S., **Rieke**, C. A., and **Brown**, W. G., 1941, *J. Amer. Chem. Soc.*, **63**, 41.
Plattner, Pl. A., 1941, *Helv. Chim. Acta*, **24**, 283 ; 1951, *Ibid.*, **34**, 971.
Plattner, Pl. A., and **Heilbronner**, E., 1948, *Helv. Chim. Acta*, **31**, 804.
Pullman, B., **Mayot**, M., and **Berthier**, G., 1950, *J. Chem. Phys.*, **18**, 257.
Wheland, G. W., and **Mann**, D. E., 1949, *J. Chem. Phys.*, **17**, 264.

Radioactive Gold Isotopes

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ABSTRACT. The half-lives, mass assignments and radiation characteristics of three neutron-excess gold isotopes have been determined as follows :

	^{200}Au	^{201}Au	^{203}Au
Half-life	48 min	26 min	55 sec
Max. β-energy (Mev)	2·2	1·5	1·9
γ-energy (Mev)	0·39, 1·13	0·55	0·69

§ 1. INTRODUCTION

The only stable gold isotope is ^{197}Au. ^{198}Au and ^{199}Au are well known, and have half-lives of 2·69 and 3·3 days respectively (National Bureau of Standards 1950). Sherr, Bainbridge and Anderson (1941) produced a 48-minute isotope by a (n, p) reaction on mercury, and Maurer and Ramm (1942) found the same by a (n, α) reaction on thallium. Its mass number is therefore 200 or 202. Butement (1951) found a new 27-minute isotope produced by a (γ, p) reaction on mercury, and therefore of mass number 201 or 203. Its radiation characteristics were not determined. This paper describes work directed towards clarifying the properties of all the gold isotopes with mass numbers 200 to 204 inclusive.

§ 2. PRODUCTION OF GOLD ISOTOPES

The isotopes were produced by the appropriate irradiations of mercury metal or thallium nitrate. The stable isotopes of these elements are as follows (National Bureau of Standards 1950):

Mercury	196	198	199	200	201	202	204
Abundance (%)	0·16	10·0	16·9	23·1	13·2	29·7	6·8
Thallium	203		205				
Abundance (%)	29·5		70·5				

Fast neutrons were produced in the cyclotron by proton bombardment of a beryllium target. 20 Mev protons gave neutrons, with energies up to 18 Mev, which were used to produce (n, p) reactions in mercury and (n, α) reactions in thallium. By increasing the proton energy up to 50 Mev, neutrons with energies up to 48 Mev were produced, and used to initiate also (n, pn) and (n, αn) reactions. X-rays of maximum energy 28 Mev, obtained from an electron synchrotron, were used to produce (γ, p) reactions in mercury.

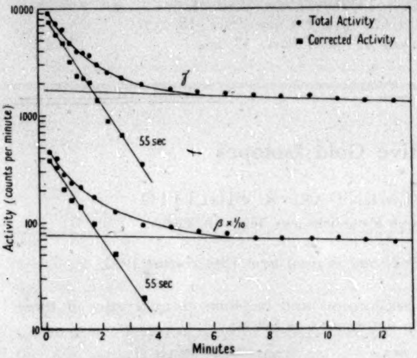

Fig. 1. Beta and gamma decay of ^{203}Au.

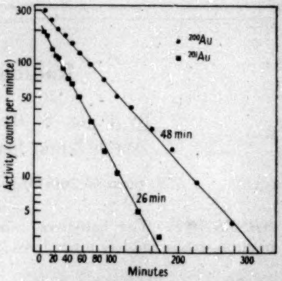

Fig. 2. Decay of gold isotopes from (γ, p) reactions on enriched mercury isotopes.

Except as described below, separation and purification of the gold isotopes from other activities were carried out by conventional radiochemical methods. The following half-lives were found for the gold isotopes by analysis of the decay curves.

Mercury (n, p). 26 minutes, 48 minutes, and approximately 3 days, the latter explicable as a mixture of ^{198}Au and ^{199} Au. There was no period less than 26 minutes except the tail end of a period of about 25 seconds which could just be observed in samples isolated very rapidly. This activity was not studied in detail, but its probable assignment is discussed at the end of this section.

Mercury (n, pn) *plus* (n, p). The above periods and also a 55-second activity (fig. 1). This new short period first appeared when the maximum neutron energy was raised to 23 Mev, and the yield, compared with that of the 26-minute activity, increased as the neutron energy was raised successively to 28, 38 and 48 Mev.

Mercury (γ, p). 55 seconds, 26 minutes, 48 minutes and 3 days. A full radiochemical identification of the 55-second activity as gold was not possible in the time available. This activity was prepared by irradiating very pure mercury which was then poured on to a few milligrams of gold foil, distilled off, and the residue heated to redness, thus leaving only gold and platinum. Consideration of the yield, which was comparable to that of the other radioactive gold isotopes showed that the 55-sec activity must arise from a (γ, p) reaction, since in this region of atomic number (γ, α) reactions leading to platinum, although just possible energetically, have a yield which is normally less than one hundredth that of (γ, p) reactions.

Thallium (n, α). 48 minutes.

Thallium $(n, \alpha n)$ *plus* (n, α). 26 minutes, 48 minutes and 3 days, the latter showing the radiation characteristics of ^{199}Au.

Each of the above periods showed both beta and gamma activity. From the modes of production the following mass assignments can be deduced: ^{200}Au 48 minutes, ^{201}Au 26 minutes, ^{203}Au 55 seconds.

These assignments were confirmed by studying the gold isotopes produced by (γ, p) reactions on enriched mercury isotopes. The concentrations (per cent) of the important mercury isotopes were as follows:

Mass number	200	201	202	204
Enriched ^{201}Hg	11·8	57·9	21·1	2·0
Enriched ^{202}Hg	3·8	1·8	91·5	1·7
Enriched ^{204}Hg	4·8	2·7	15·7	72·3

The yields for the three short period activities were computed after correction for decay during irradiation and processing, and compared with the results for natural mercury.

Enriched ^{201}Hg gave mainly a 48-minute gold (^{200}Au, fig. 2), the ratio of the yields of the 48-minute to the 26-minute activities being six times greater than the ratio from natural mercury, an increase in agreement with the change in the ratio of the concentrations of ^{201}Hg and ^{202}Hg. Enriched ^{202}Hg gave a nearly pure 26-minute gold (^{201}Au, fig. 2), the 48-minute activity being too small for accurate estimation, as might be expected, since the concentration of ^{201}Hg was only 1·8%. Enriched ^{204}Hg gave mainly the 55-second activity (^{203}Au), the 26-minute activity being too weak for very accurate measurement.

A possible explanation of the absence of any period for ^{202}Au, which must be produced in large yield both by Hg (n, p) and Tl (n, α), would be that it has a half-life almost equal to that of 48-minute ^{200}Au. This explanation was shown to be untenable by irradiating equal weights of enriched ^{202}Hg and natural mercury, for 20 minutes with 18 MEV neutrons under the same experimental conditions. The cyclotron beam current was constant during each irradiation, and a small correction was made for a change in the integrated neutron flux, as measured by the activities induced in standard copper monitor foils. The gold activities were quantitatively isolated and the 48-minute activity from enriched mercury was only 0·18 of that from natural mercury. This was to be expected if this activity derived only from a (n, p) reaction on the ^{200}Hg present, the predicted ratio in this case being $3{\cdot}8/23{\cdot}1 = 0{\cdot}16$. If a 48-minute activity were also produced from ^{202}Hg with a similar reaction cross section, the total yield from enriched mercury would have been greater than that from natural mercury by a factor of about $(91{\cdot}5 + 3{\cdot}8)/(29{\cdot}7 + 23{\cdot}1) = 1{\cdot}8$.

The decay energies of ^{202}Au and ^{204}Au calculated from the semi-empirical Fermi formula tabulated by Metropolis and Reitwiesner (1950) are 2·6 and 3·3 MEV respectively. Using the graphs of Feenberg and Trigg (1950) relating log*f* with beta-decay energy, and a possible log*ft* value of 5·0, the calculated half-lives of these two isotopes could be 20 and 10 seconds respectively. The 25-second activitv is probably due to one of these isotopes.

§ 3. RADIATION

The gamma-radiation was studied with the conventional type of scintillation spectrometer (NaI-Tl crystal), the pulses being displayed on an oscillograph and photographed. The sources were prepared by the neutron or X-ray irradiation of mercury, and photographs were taken at regular intervals in order to follow the fading out of individual components according to the half-lives of the isotopes responsible. The results for the gamma-ray energies were: ^{200}Au 1·13 and 0·39, ^{201}Au 0·55 and ^{203}Au 0·69 Mev.

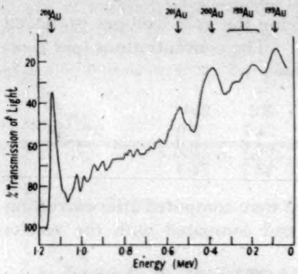

Fig. 3. Microphotometer trace taken across negative photograph of oscillograph screen of gamma scintillation spectrometer.

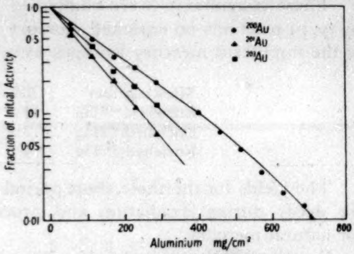

Fig. 4. Absorption of beta-radiation of gold isotopes.

Figure 3 shows the record obtained by scanning with a microphotometer across a photograph taken just after the ^{203}Au had decayed away. There are peaks corresponding to the radiations from ^{200}Au and ^{201}Au, a broad peak due to the combined effect of the 0·156, 0·207 and 0·23 Mev gamma-rays of ^{199}Au (Beach, Peacock and Wilkinson 1949) and a peak at about 75 kev attributable to the combined effect of the 70 kev gamma-ray and the mercury K X-rays from ^{199}Au. The relative intensity of the low energy radiations is much exaggerated by the increased efficiency of the counter in this region. The pulses in the region 0·6 to 1·0 Mev are, in part at least, due to the Compton electrons from the 1·13 Mev gamma-ray, but there may also be superimposed the effect of one or more weak gamma-rays from ^{200}Au.

The beta-particle energy was determined by the usual technique of absorption in aluminium. For each isotope calculated corrections were made for the effect of the longer lived isotopes present. For ^{203}Au a separate sample was used to obtain each point on the graph (fig. 4). Because of necessary corrections only the initial part of each absorption curve could be accurately determined. From a knowledge of the efficiencies of the beta and gamma counters, it was estimated that only about 20% of the beta-particle emission of ^{200}Au is accompanied by gamma-rays, assuming the two gamma-rays are not in cascade. The corresponding value for ^{201}Au was 5%, and for ^{203}Au 10%. A reasonable approximation to the maximum beta-particle energy could therefore be obtained by using the nomogram of Behrens (1950) relating the absorption in aluminium with the energy of a simple beta-emitter.

The results for the beta-particle energies were ^{200}Au 2·2, ^{201}Au 1·5, ^{203}Au 1·9 MEV. The value of Sherr *et al.* (1941) for ^{200}Au was 2·5 MEV.

ACKNOWLEDGMENTS

Acknowledgments are made to members of the cyclotron group for carrying out irradiations, and to the Director, Atomic Energy Research Establishment, for permission to publish these results.

REFERENCES

BEACH, L. A., PEACOCK, C. L., and WILKINSON, R. G., 1949, *Phys. Rev.*, **76**, 1585.
BEHRENS, D. J., 1950, Atomic Energy Research Establishment Report T/M 6.
BUTEMENT, F. D. S., 1951, *Proc. Phys. Soc.* A, **64**, 395.
FEENBERG, E., and TRIGG, G., 1950, *Rev. Mod. Phys.*, **22**, 399.
MAURER, W., and RAMM, W., 1942, *Z. Phys.*, **119**, 602.
METROPOLIS, N., and REITWIESNER, G., 1950, *Table of Atomic Masses*, N.P. 1980 (Oak Ridge, Tennessee : U.S. Atomic Energy Commission).
NATIONAL BUREAU OF STANDARDS, 1950, *Nuclear Data*, N.B.S. Circular 499.
SHERR, R., BAINBRIDGE, K. T., and ANDERSON, H. H., 1941, *Phys. Rev.*, **60**, 473.

LETTERS TO THE EDITOR

Spin–Orbit Coupling in the D–D Reaction

It is well known that the observed angular distribution of the outgoing particles in the D–D reaction cannot be accounted for adequately without the introduction of strong spin–orbit coupling (Beiduk *et al.* 1950, to be referred to as BPK). This has resulted in the suggestion that, because of such coupling, the outgoing particles may be polarized (Blin-Stoyle 1951, Cini 1951). Recently this possibility has been confirmed both for outgoing neutrons and protons (Bishop *et al.* 1952, Langley *et al.* 1952*); in particular at deuteron energies of 300 kev the proton polarization appears to be about 30%.

A theoretical expression for the polarization at energies up to about 300 kev (when only incoming S, P and D waves need be considered) can be written

$$\mathbf{P}(\theta)=\mathbf{n}C\,\frac{A(E)\sin\theta\cos\theta}{1+A(E)\cos^2\theta}, \qquad \ldots\ldots(1)$$

where θ defines the direction of motion of the outgoing particles in the centre of mass system and $\mathbf{n}$ is a unit vector normal to the plane of the reaction. $A(E)$ is the energy dependent asymmetry factor occurring in the angular distribution as the coefficient of $\cos^2\theta$. C can be written in the notation of BPK as

$$C=-6i\mathscr{I}\left[(\gamma_{10}{}^{1})^*(\gamma_{11}{}^{0}+\beta_{11}/\sqrt{2})+(\gamma_{10}{}^{0})^*(\gamma_{11}{}^{-1})+\frac{1}{\sqrt{6}}(\beta_{12})^*\left(3\gamma_{11}{}^{0}-2\gamma_{11}{}^{-1}+\frac{1}{\sqrt{2}}\beta_{11}\right)-\sqrt{\frac{5}{54}}\,\alpha_0{}^*\beta_2\right]\Big/[A_1+\tfrac{1}{3}A_{02}]. \qquad \ldots\ldots(2)$$

BPK attempted to calculate values for the various matrix elements occurring in C with the assumption that tensor forces alone were responsible for the spin–orbit coupling. Under these circumstances (2) reduces to

$$C=5\sqrt{6}\,|\beta_{12}|\,|\gamma_{11}{}^{0}|\sin\phi/(A_1+\tfrac{1}{3}A_{02}), \qquad \ldots\ldots(3)$$

where ϕ is the phase difference between β_{12} and $\gamma_{11}{}^{0}$.

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* Prof. P. Huber has very kindly informed us that similar results have been obtained in Basel.

Assuming their calculated values for $|\beta_{12}|$ and $|\gamma_{11}{}^0|$ it is found that at 300 kev the maximum possible value of the polarization is about 7%, which is considerably less than the experimentally determined value.

This fact can be interpreted in two ways : either (*a*) tensor forces alone are insufficient to account for the spin–orbit coupling, or (*b*) the theory of BPK is too crude to give reasonable values for the matrix elements.

In case (*a*) internucleonic forces having a spin dependence of the form $L_{ij}(\sigma_i+\sigma_j)$ might be acting (such forces have been used fairly successfully in explaining nucleon–nucleon collision phenomena (Case and Pais 1950)). Using the same method as BPK for such an interaction yields the following expression for C

$$C=-6i\mathscr{I}\left[2(\gamma_{10}{}^1)^*(\gamma_{11}{}^{-1})-\sqrt{\frac{5}{54}}\alpha_0{}^*\beta_2\right]\Big/(A_1+\tfrac{1}{3}A_{02}). \qquad \ldots\ldots(4)$$

It is then easy to show that values can be given to the various matrix elements which, whilst being consistent with the observed angular distribution, also easily account for the magnitude of the polarization.

In case (*b*) the expression (3) might still be retained since it results mainly from symmetry arguments. An attempt can then be made to choose values for $|\beta_{12}|$, $|\gamma_{11}{}^0|$ and ϕ which will account for the form of the angular distribution and the sign and magnitude of the polarization. In this connection the behaviour of K_1 (see BPK), which reflects the effect of spin–orbit coupling on the angular distribution and total cross section, is of considerable interest.

If only central and tensor forces are effective K_1 is given by

$$K_1=6|\gamma_{11}{}^0|^2+|\beta_{12}|^2-2\sqrt{6}|\beta_{12}||\gamma_{11}{}^0|\cos\phi, \qquad \ldots\ldots(5)$$

and, according to BPK, should be energy independent. Its value can be determined from the measured partial and total cross sections. In practice, slightly better agreement with the experimental results for outgoing protons is obtained if K_1 is assumed to vary with energy. This energy dependence can be explained if the fact that the outgoing F-waves (implied by β_{12}) have to penetrate a potential barrier is taken into account. We therefore write $\beta_{12}=P_3{}^{1/2}\beta_{12}'$ where the penetrability P_3 is calculated by standard methods.

Thus

$$K_1=6|\gamma_{11}{}^0|^2+|\beta_{12}'|^2P_3-2\sqrt{6}|\beta_{12}'||\gamma_{11}{}^0|\sqrt{P_3}\cos\phi. \qquad \ldots\ldots(6)$$

Ignoring the variation of $P_3{}^{1/2}$ with energy (which is very slow) and taking a mean value $\overline{P}_3{}^{1/2}$, we can write

$$K_1=X+P_3Y, \qquad \ldots\ldots(7)$$

where $X=6|\gamma_{11}{}^0|^2-2\sqrt{6}|\beta_{12}'||\gamma_{11}{}^0|\overline{P}_3{}^{1/2}\cos\phi$; $Y=|\beta_{12}'|^2$ and are taken to be energy independent.

Using all ‘ thin target ’ published results it is found that a good fit with experiment is obtained if $X=0{\cdot}024$ and $Y=0{\cdot}087$.

Further, to account for the sign and magnitude of the proton polarization $C=0{\cdot}75$.

Such values of X, Y and C can be obtained by choosing $|\gamma_{11}{}^0|=0{\cdot}185$, $|\beta_{12}{}^2|=0{\cdot}295$, and $\phi=12°\ 35'$.

These values should not be taken too seriously since there are large errors on the values of X and Y. The results do indicate, however, that tensor forces alone may well be sufficient to account for the spin–orbit coupling necessary to produce the observed polarization. If, subsequently, more quantitative theories show that this is not the case we have seen that a non-central force of the **L . S** variety might satisfy the requirements.

The author would like to express his thanks to Mrs. M. Owen who investigated the fitting of K_1 with experiment and to the Pressed Steel Co. Ltd. for a research fellowship.

Clarendon Laboratory,
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7th August 1952.

R. J. Blin-Stoyle.

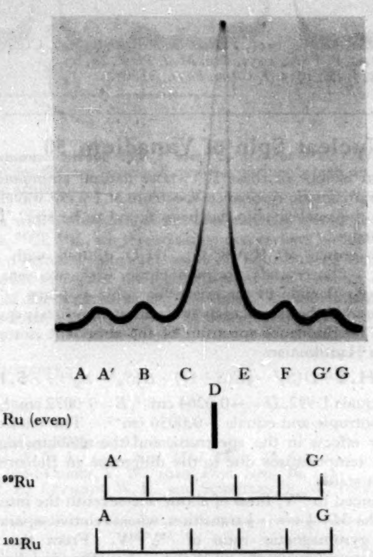
Beiduk, F. M., Pruett, J. R., and Konopinski, E. J., 1950, *Phys. Rev.*, **77**, 622.
Bishop, G. R., Westhead, J. M., Preston, G., and Halban, H., 1952, *Nature, Lond.*, **170**, 113.
Blin-Stoyle, R. J., 1951, *Proc. Phys. Soc.* A, **64**, 700.
Case, K. M., and Pais, A., 1950, *Phys. Rev.*, **80**, 203.
Cini, M., 1951, *Nuovo Cim.*, **8**, 1.
Langley, H. J., Little, R. N., and Slye, J. M., 1952, *Phys. Rev.*, **86**, 419.

The Nuclear Spins of ^{99}Ru and ^{101}Ru

The paramagnetic resonance spectrum from a crystal of $Ru(NH_3)_6Cl_3$ diluted with the diamagnetic salt $Co(NH_3)_6Cl_3$ has been measured at a wavelength of 1·2 cm and a temperature of 20° K. The hyperfine structure indicates that the nuclear spins of ^{101}Ru and ^{99}Ru are both 5/2, and that the ratio of their magnetic moments (101 : 99) is $1{\cdot}09 \pm 0{\cdot}03$.

Trivalent ruthenium has five electrons in the 4d shell and is analogous to trivalent iron in the 3d transition group. The spectrum and the magnetic behaviour of the $Ru(NH_3)_6$ complex will not be discussed in detail here, but briefly the behaviour seems to be consistent with that expected from a very strongly bound complex (Van Vleck 1935), the ground state being a Kramers doublet and the effective spin ½, which is a similar situation to that found in a ferricyanide.

The hyperfine structure (see figure) has been resolved by diluting $Ru(NH_3)_6Cl_3$ with the diamagnetic salt $Co(NH_3)_6Cl_3$ in the ratio Ru : Co $\sim$ 1 : 200. The overall line width at 20° K is then about 25 gauss. Since a width approaching 20 gauss is to be expected from the field of the eighteen protons in the $Ru(NH_3)_6$ cluster, any appreciable improvement in the resolution could probably only be obtained by using deuterium rather than hydrogen in the ammonia. In the figure the strong line is attributed to the even isotopes of ruthenium (Ru 96, 98, 100, 102, 104, total abundance 70·21%), and the satellites to ^{99}Ru (12·81%) and ^{101}Ru (16·98%). These abundances are given by Engelkemeir (1944). The satellites consist of the outside pairs of lines AA′, G′G which can just be resolved, suggesting that these are from the two odd isotopes. The inner lines B and F are of the same total intensity (area under curve) as the outside pairs, within the experimental error, suggesting that these are also from both isotopes, but are unresolved. There is no sign of any hyperfine structure outside A and G. It is therefore concluded that the spins of both odd isotopes are $I=5/2$, $[(2I+1)$ lines from each$]$. Also the overall hyperfine separation AG of the most abundant isotope (^{101}Ru) is seen to be slightly greater than that of ^{99}Ru (A′G′), giving the ratio of the nuclear magnetic moments $\mu_{101}/\mu_{99} = 1{\cdot}09$.



The usual shell model scheme suggests that the ground states of ^{99}Ru and ^{101}Ru should be $4d_{5/2}$ and $5g_{7/2}$ respectively. However, as pointed out by Klinkenberg (1952), there is some evidence that the $5g_{7/2}$ shell for odd neutrons fills in pairs, and he proposes that ^{99}Ru with 55 neutrons may have 50 neutrons in closed shells with the remaining five in the configuration $5g_{7/2}(4)$, $4d_{5/2}(1)$, while ^{101}Ru has its remaining seven in the configuration $5g_{7/2}(6)$, $4d_{5/2}(1)$. The present measurements are consistent with this proposal.

Paramagnetic resonance has also been observed in $K_3[Mo(CN)_8]$; $K_3[MoCl_6]$; $K_2[MoCl_5H_2O]$; $[Ru(NH_3)_6]Cl_3$, $3HgCl_2$; $[Ru(NH_3)_6]Cl_3$ (concentrated); and in a mixed crystal of $(NH_4)_2[IrCl_6]$ and $(NH_4)_2[PtCl_6]$. Investigations are being continued in these and other compounds of the Pt and Pd group elements.

It was not easy to find a suitable ruthenium compound for this experiment, and it is a pleasure to thank Dr. Powell and Mr. Lever of Messrs. Johnson, Matthey & Co. Ltd. both for their valuable advice on the chemical side, and for supplying the ruthenium compound.

Clarendon Laboratory,
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6th August 1952.

J. H. E. Griffiths.
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Engelkemeir, D. W., 1944, Plutonium Project Report, CC.1959.
Klinkenberg, P. F. A., 1952, *Rev. Mod. Phys.*, **24**, 63.
Van Vleck, J. H., 1935, *J. Chem. Phys.*, **3**, 807.

Nuclear Spin of Vanadium 50

Vanadium contains an isotope of mass 50, whose natural abundance is about 0·2%. By observation of the paramagnetic resonance spectrum at 1·3 cm wavelength of a sample enhanced to about 20%, the nuclear spin has been found to be six. This is the highest nuclear spin yet established.

Single crystals were grown of $K_4V(CN)_6 . 3H_2O$ diluted with the isomorphous diamagnetic ferrous salt. The crystals are monoclinic, with two ions in unit cell, one derived from the other by reflection in the crystallographic *ac*-plane. The vanadous ion is in a $3d^3$ state, and in the solid the orbital motion is almost completely quenched, leaving an effective spin $S=3/2$. The resonance spectrum of the abundant isotope, ^{51}V (for which $I=7/2$), can be fitted to a Hamiltonian

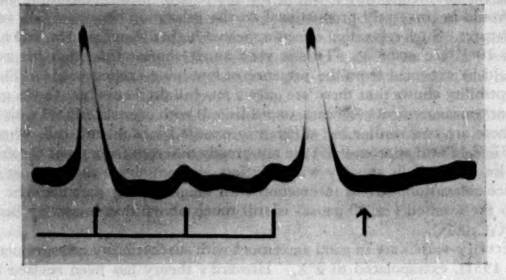
$$\mathscr{H}=g\beta \mathbf{H}.\mathbf{S}+D\{S_z^2-\tfrac{1}{3}S(S+1)\}+E\{S_x^2-S_y^2\}+A\mathbf{S}.\mathbf{I},$$

where g is isotropic and equals 1·992, $D=-0{\cdot}0264$ cm^{-1}, $E=0{\cdot}0072$ cm^{-1}, and the hyperfine structure constant A is isotropic and equals $-0{\cdot}0056$ cm^{-1}. The relative signs are determined from second-order effects in the spectrum, and the absolute sign of D from the intensity variation at low temperatures due to the difference in Boltzmann factors of the uppermost and lowermost states.

With the sample enhanced in ^{50}V, lines of about one-seventh the intensity of those due to ^{51}V were observed for the $M=\frac{1}{2}\longleftrightarrow-\frac{1}{2}$ transition, whose relative separation corresponded to the known nuclear gyromagnetic ratio of ^{50}V/^{51}V. From the frequency ratios (^{50}V/^{2}D) and (^{51}V/^{1}H) given respectively by Walchli, Leyshon and Scheitlin (1952) and Knight and Cohen (1949) the ratio (^{50}V/^{51}V) is 0·3792, and we find the ratio of the hyperfine structure constants A_{50}/A_{51} to be $0{\cdot}380\pm0{\cdot}001$. More accurate measurements of this ratio would be of interest to determine whether there is a nuclear volume effect, as, according to the theory of Abragam (1951), the hyperfine structure is due entirely to s-electrons, through admixture of the $3s3p^63d^34s$ state.

The figure shows two weak lines, corresponding to the nuclear magnetic quantum numbers 5 and 6, of ^{50}V, situated between the strong lines $m=3/2$, $5/2$ of ^{51}V. Since the hyperfine structure lines are very nearly equally spaced, it is clear that there is no line corresponding to $m=8$ for ^{50}V, and the principal question was whether a line corresponding to $m=7$ would be resolved from the strong $m=5/2$ line of ^{51}V. The position which such a line would occupy is indicated by the arrow in the figure, and it seems certainly to be absent. To check this point, experiments will be carried out at 3 cm wavelength, when a ^{50}V, $m=7$ line would be further displaced from the ^{51}V, $m=5/2$ line. This arises from second-order effects which displace the lines downwards in field by $(A^2/2h\nu)\{I(I+1)-m^2\}$. The displacement is different for the two isotopes, and at 3 cm wavelength an $m=7$ line would be as well resolved as the $m=6$ line shown in the figure at 1·3 cm. From other second-order effects it should be possible to check the positive sign for the nuclear moment of ^{50}V obtained by Walchli, Leyshon and Scheitlin.

For ^{50}V, $(Z=23, N=27)$ the odd proton and odd neutron should be both in $f_{7/2}$ states. The observed spin $I=6$ illustrates a tendency for the spins of odd–odd nuclei not to take the extreme values which the states of the odd particles would permit. Previous examples are ^{6}Li, ^{22}Na, ^{24}Na, ^{38}Cl, ^{40}K, while (excluding cases where both odd particles are in $\frac{1}{2}$ states) only ^{10}B, ^{86}Rb have extreme values (cf. table II, Klinkenberg 1952).



Spectrum of vanadium. Strong lines: $m=5/2$, $3/2$ for ^{51}V. The weak lines $m=6$, 5, 4 (right to left) for ^{50}V are indicated, and the position which an $m=7$ line would occupy is shown by the arrow.

The authors wish to record their gratitude to the Director and the Electromagnetic Separator Group of the Atomic Energy Research Establishment, Harwell, who supplied the enhanced vanadium, and to Dr. P. F. D. Shaw, who converted it to the desired chemical form.

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Oxford.
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J. M. Baker.
B. Bleaney.

Abragam, A., 1951, *Physica*, **17**, 209.
Klinkenberg, P. F. A., 1952, *Rev. Mod. Phys.*, **24**, 63.
Knight, W., and Cohen, V. W., 1949, *Phys. Rev.*, **76**, 1421.
Walchli, H. E., Leyshon, W. E., and Scheitlin, F. M., 1952, *Phys. Rev.*, **85**, 922.

Paramagnetic Resonance in Potassium Ferricyanide

Potassium ferricyanide, $K_3Fe(CN)_6$, has long been of considerable interest because of its anomalous magnetic properties. Unlike most ferric compounds, which show an isotropic susceptibility characteristic of the $3d^5$, ^6S state, the cyanide has a much smaller and very anisotropic susceptibility. Pauling (1939) has explained the small susceptibility on the hypothesis of covalent bonding, the set of octahedral bonds d^2sp^3 to the six cyanide groups using up two of the 3d orbitals. Thus only three d-orbitals are available for the electrons which normally go in the 3d shell. These are completely filled by six electrons, making potassium cobalticyanide and potassium ferrocyanide diamagnetic. With only five electrons, the single hole remaining in the 3d shell gives a susceptibility equal to that for $S=\frac{1}{2}$, with an orbital contribution. Van Vleck (1935) has shown that a similar result can be obtained by crystal field theory, and Howard (1935) has attempted to fit the anisotropic susceptibility using a rhombic component of the crystalline field comparable in magnitude with the spin–orbit coupling.

Potassium ferricyanide grows in monoclinic, pseudorhombic crystals, and resonance was detected at 20° K. In the concentrated salt a single resonance line is found, corresponding to a spin $S=\frac{1}{2}$, which reaches extreme positions along the rhombic axes. The g-values are: a-axis, 2·30; b-axis, 2·18; c-axis, 0·94. Here the accuracy ($\pm 0{\cdot}03$) is not very high because of the abnormally large line width. The half-width at half intensity due to magnetic dipole interaction with neighbouring ferric ions should be less than 0·2 kG, but the smallest observed width (along the a-axis) was 0·8 kG, while along the b- and c-axes it was over 1·5 kG. The line-width did not change on pumping down to 12° K, showing that the anomalous line width is not due to spin–lattice relaxation, since then the line width would be inversely proportional to the relaxation time τ, which varies rapidly with temperature. Such relaxation effects appear at higher temperatures, and τ is estimated as about 2×10^{-10} sec at 62° K. This is very much shorter than that for normal ferric salts, as would be expected from the presence of low-lying excited levels. The behaviour of the susceptibility shows that these are only a few hundred cm^{-1} above the ground state.

Preliminary measurements (Bowers, unpublished) with crystals diluted with $K_3Co(CN)_6$ show that there are two similar but differently oriented ions in unit cell, whose principal g-values (2·37, 2·11 and approx. 0·85) are not greatly different from those for the crystalline axes. The line width falls steadily with dilution, showing again that it must be due, not to spin–lattice relaxation, but to interaction with neighbouring paramagnetic ions. The minimum so far reached ($\simeq 30$ gauss) is still much above that found by Bowers (1952) for diluted $K_3Cr(CN)_6$.

The observed g-values are in good agreement with susceptibility measurements (Jackson 1938, Guha 1951), extrapolated to 0° K. Howard's theory has been revised by Bersohn (1949), who finds that if the g-values for the a- and b-axes are fitted, that for the c-axis comes to 1·5. We find that the closest fit to all the principal g-values that can be obtained is the set (2·55, 2·27, 0·98). Fair agreement can then be obtained with the susceptibility measurements if the spin–orbit coupling coefficient is taken as about 390 cm^{-1}, which is only 10% lower than the estimate of Kotani (1949). The fact that the theoretical g-values are slightly too high is due to the approximations in the theory.

Preliminary measurements by Baker (unpublished) show that the g-values of the isoelectronic ion Mn^{2+} in $K_4Mn(CN)_6 \cdot 3H_2O$, diluted with the isomorphous diamagnetic ferrous salt, show a similar anisotropy. The line width also seems abnormally great along the direction of the lowest g-value. On the other hand, diluted crystals of $K_4V(CN)_6 \cdot 3H_2O$ show a normal spectrum with very narrow lines. Thus the anomalous behaviour of the $(3d)^5$ ions (Mn^{2+}, Fe^{3+}) is in marked contrast with the normal behaviour of the $(3d)^3$ ions (V^{2+}, Cr^{3+}). The magnetic properties of the latter depend little on whether they are ionically or covalently bound, while those of the former are strongly affected.

Our thanks are due to Mr. J. M. Baker and Mr. K. D. Bowers for allowing us to quote unpublished work.

Clarendon Laboratory,
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27th August 1952.

B. Bleaney.
D. J. E. Ingram.

Bersohn, R., 1949, *Thesis*, Harvard University.
Bowers, K. D., 1952, *Proc. Phys. Soc.* A, in the press.
Guha, B. C., 1951, *Proc. Roy. Soc.* A, **206**, 353.
Howard, J., 1935, *J. Chem. Phys.*, **3**, 813.
Jackson, L. C., 1938, *Proc. Phys. Soc.*, **50**, 707.
Kotani, M., 1949, *J. Phys. Soc., Japan*, **4**, 293.
Pauling, L., 1939, *The Nature of the Chemical Bond* (Ithaca, New York: Cornell University Press).
Van Vleck, J. H., 1935, *J. Chem. Phys.*, **3**, 807.

The 'Extra' Levels in Rare Earth Salts

Interpretations of the optical absorption spectra of rare earth crystals have sometimes shown that there are more low-lying levels than can be accounted for by assuming splittings by a crystal field (see Yost, Russell and Garner 1947 for a survey). It has been suggested that these may be due to a coupling between the electronic states and thermal vibrations. We would like to put forward evidence which points to another explanation.

We suggest that the levels may be created by the electrostatic fields in the crystals, but that the fields are not quite the same for all the ions. Thus the absorption spectra may be a superposition of the individual, slightly different, spectra. Magnetic resonance results on samarium ethyl sulphate would seem to require an explanation of this sort. It has been observed that a number of crystals, both concentrated and diluted with lanthanum ethyl sulphate, show two resonance lines with very similar *g*-values. The weaker of the two lines varies considerably in intensity from one crystal to another, and in fact it is possible to find crystals which show only one line. (A crystal of this last sort was used in obtaining the previously reported measurements by Bogle and Scovil (1952).) When the crystal was rotated in the magnetic field, the two lines, when present, did not cross as would be expected if the crystal was twinned. Also the absence of twinning was confirmed by the spectra of gadolinium and neodymium impurities, which were not doubled. There were thus two samarium ions with very similar ground states. A similar phenomenon has been reported in cobalt fluosilicate (Bleaney and Ingram 1951).

Most of the optical absorption measurements seem to have been made on conglomerates. It would therefore be of considerable interest to make measurements on a number of single crystals to see if there are still too many levels. This work might then be followed by resonance measurements on the same crystals.

Clarendon Laboratory,
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25th August 1952.

H. E. D. Scovil.
K. W. H. Stevens.

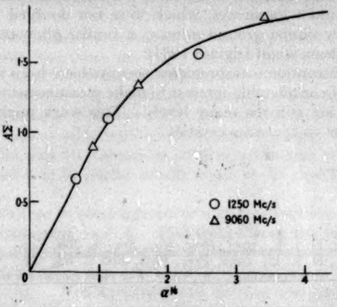
Bleaney, B., and Ingram, D. J. E., 1951, *Proc. Roy. Soc.* A, **208**, 143.
Bogle, G. S., and Scovil, H. E. D., 1952, *Proc. Phys. Soc.* A, **65**, 368.
Yost, D. M., Russell, H., and Garner, C. S., 1947, *The Rare Earth Elements and Their Compounds* (New York: Wiley).

The Mean Free Path of Conduction Electrons in Bismuth

It has recently been pointed out by Sondheimer (1952) that in metals containing a very small number of conduction electrons, such as bismuth, the electronic mean free path l should be abnormally long, of the order of $1\,\mu$ at room temperature, because the requirements of momentum and energy conservation forbid collisions between the electrons and the higher-energy phonons. The experimental results of Eucken and Förster (1934) on the apparent resistivity of thin bismuth wires in fact indicate a mean free path at room temperature of about $7\,\mu$, while those of Justi, Kohler and Lautz (1951) on the thermoelectric power of thin bismuth films give a value of about $0{\cdot}2\,\mu$. The discrepancy between these values may be due partly to the intrinsic difficulty, in thin-conductor measurements, of ensuring that the properties of the material are the same as those of the bulk metal; it should also be noted that the value deduced from the experiments of Justi *et al.* depends critically on the way in which l is assumed to vary with the energy of the electron. In view of the discrepancy between these values, further data seem desirable.

It has been found that measurements on the ' anomalous skin effect ' in metals will yield reliable estimates of the temperature-independent quantity σ/l, where σ is the d.c. conductivity, and hence of l at any temperature. The quality factor Q of a resonant specimen is plotted against $\sigma^{1/2}$ (σ being varied by varying the temperature), and the resulting curve compared with the theoretical curve (Reuter and Sondheimer 1948) of $A\Sigma$ plotted against $\alpha^{1/6}$, where $A\Sigma \propto Q$ and $\alpha^{1/6}=(3\pi\omega/10^9)^{1/6}(\sigma/l)^{-1/6}\sigma^{1/2}$; here ω is the angular frequency and σ is measured in ohm^{-1} cm^{-1}. Thus σ/l can be found from the parameters fitting the experimental to the theoretical curve.

Measurements have been made on bismuth at two frequencies, 1250 and 9060 Mc/s, and at three temperatures, 290°K, 80°K and 4°K, using the techniques described elsewhere (Pippard 1947, 1950, Chambers 1950, 1952). The 1250 Mc/s specimen was in the form of a single-crystal ' hairpin ' of wire about 6 cm long (cast in a silica tube), forming a shorted quarter-wave resonator; a section from one limb of this specimen was used as a half-wave resonator at 9060 Mc/s. The triad axis of the crystal was perpendicular to the specimen axis. The residual resistivity at 4°K was about 0·07 times the room-temperature value. Because of the high resistivity of bismuth the resonators had rather low values of Q, which restricted the accuracy of the measurements. The figure shows the observations fitted to the theoretical curve of Reuter and Sondheimer ; it is assumed that on colliding with the surface of the metal the electrons are reflected diffusely rather than specularly (cf. Chambers 1950, 1952). The same value of σ/l has been used in fitting the results at both frequencies, namely $2{\cdot}74\times10^{7}$ ohm^{-1} cm^{-2}, corresponding to a value of l at room temperature of 3·4 μ. These figures differ considerably from those for normal metals ; for example, for copper the value of σ/l (found by the same technique) is $1{\cdot}54\times10^{11}$ ohm^{-1} cm^{-2}, corresponding to a room-temperature value for l of 0·038 μ.



Experimental results fitted to theoretical (Reuter and Sondheimer) curve.

The estimates for σ/l and l are subject to the following uncertainties : (i) There is a possible error of ± 20% due simply to the low accuracy of the measured values of Q. (ii) If the surface of the specimen is imperfect, the value of σ/l will be an underestimate and therefore that of l an overestimate. Under the microscope the specimen showed a good surface finish ; experience with other metals (Chambers and Pippard 1952, Chambers 1952) leads to the belief that the true value of σ/l is highly unlikely to be greater than 4×10^{7} ohm^{-1} cm^{-2} ; correspondingly the true value of l at room temperature is unlikely to be less than 2·3 μ. (iii) These figures have been deduced by comparing the experimental results with the isotropic free-electron theory of Reuter and Sondheimer. For a single crystal, the values of σ/l and l obtained in this way depend on orientation and probably represent average values for electrons travelling at small angles to the surface (Pippard 1950, Chambers 1952) : the values given above are therefore probably weighted in favour of electrons travelling perpendicular to the triad axis.

It is concluded that, in agreement with Sondheimer's suggestion, the mean free path of the conduction electrons in bismuth is much longer than in normal metals, and that (for electrons travelling perpendicular to the triad axis) it probably lies between 2 and 4 μ at room temperature.

Royal Society Mond Laboratory,
Cambridge.
18th August 1952.

A. B. Pippard.
R. G. Chambers.

Chambers, R. G., 1950, *Nature, Lond.*, **165**, 239 ; 1952, to be published.
Chambers, R. G., and Pippard, A. B., 1952, *Symposium on Properties of Metallic Surfaces* (London : Institute of Metals), p. 281.
Eucken, A., and Förster, F., 1934, *Nachr. Ges. Wiss., Göttingen*, **1**, 43.
Justi, E., Kohler, M., and Lautz, G., 1951, *Z. Naturforsch.*, **6a**, 456, 544.
Pippard, A. B., 1947, *Proc. Roy. Soc.* A, **191**, 370, 385 ; 1950, *Ibid.*, **203**, 98.
Reuter, G. E. H., and Sondheimer, E. H., 1948, *Proc. Roy. Soc.* A, **195**, 336.
Sondheimer, E. H., 1952, *Proc. Phys. Soc.* A, **65**, 561.

Zener's Treatment of Ferromagnetism

Zener (1951 I)* has suggested an interpretation of the effects of electron exchange interaction in solids which, as developed by Zener (II), (III) and (IV) and Carr (1952), appears to account for a wide range of structural and magnetic properties. The object of the present note is to consider critically the validity of this treatment.

The basic postulates introduced by Zener (I), subsequently referred to as Z (i) to (iii), are : (i) in a single atom the electrons in the incomplete d shell are in the state of maximum multiplicity; (ii) the exchange interaction between electrons in adjacent d shells favours anti-parallel setting of their spins (i.e. antiferromagnetic); (iii) exchange interaction between d shells and the conduction electrons tends to a parallel setting (i.e. ferromagnetic).

For a pure metal Zener expresses the interaction energy in the form

$$E=\tfrac{1}{2}\alpha S_d^2-\beta S_d S_c+\tfrac{1}{2}\gamma S_c^2, \qquad \ldots\ldots (1)$$

where S_d, S_c are the mean resultant spins of the d shells and conduction electrons in Bohr magnetons per atom and α, β, γ are appropriate coupling coefficients, all positive. The magnetic moment is then $\mu=S_d+S_c$.

If $\beta^2-\alpha\gamma<0$, the minimum energy equilibrium condition is $\dfrac{\partial E}{\partial S_c}=\dfrac{\partial E}{\partial S_d}=0$, giving $S_c=S_d=0$, i.e. the resultant moment is zero. If however, $\beta^2-\alpha\gamma>0$, the lowest energy occurs when either S_d or S_c, or both, attain their greatest possible value :

$$\text{for } \beta/\gamma \leqslant S_{c\,\max}/S_{d\,\max} : S_d=S_{d\,\max},\ S_c=(\beta/\gamma)S_{d\,\max} \text{ and } \mu=S_{d\,\max}(1+\beta/\gamma); \quad ..\ (2)$$

$$\beta/\alpha \leqslant S_{d\,\max}/S_{c\,\max} : S_d=(\beta/\alpha)S_{c\,\max},\ S_c=S_{c\,\max} \text{ and } \mu=S_{c\,\max}(1+\beta/\alpha); \quad ..\ (3)$$

$$\text{and } \alpha/\beta \leqslant S_{c\,\max}/S_{d\,\max} \leqslant \beta/\gamma : S_d=S_{d\,\max},\ S_c=S_{c\,\max} \text{ and } \mu=S_{c\,\max}+S_{d\,\max}. \quad ..\ (4)$$

By writing the equilibrium condition as $\dfrac{dE}{dS_c}=0$, Zener (I) obtains only case (2), but the necessary condition for this case to apply may not be satisfied generally. The validity of Zener's (III) estimate of β/γ is very doubtful, but this question will not be considered in this note. His estimate gives $\beta/\gamma \simeq \frac{1}{7}$. Since $S_{d\,\max}$ may be as large as 5, case (2) will not apply if $S_{c\,\max}$ is less than about $\frac{5}{7}$.

For Fe, Co, Ni, assuming one conduction electron per atom, $S_{d\,\max}=3, 2, 1$. Then with β/γ as calculated by Zener (III), (2) gives $=3{\cdot}45, 2{\cdot}30, 1{\cdot}17$, as compared with the corresponding experimental values of 2·22, 1·71, 0·61. Zener (III), however, assumes the number of conduction electrons per atom to be 0·22, 0·7, 0·6. These numbers are consistent with the band scheme, but it is not clear how they arise in Zener's scheme. If all the ions in the pure metal have similar d shell configurations, non-integral numbers of conduction electrons cannot arise. It is then necessary to assume that several types of d shell configuration occur (as Zener (IV) does for Fe), in which case Carr's approach (see below) is more appropriate, and the calculations in Zener (III) have no significance.

Carr (1952) considers the behaviour of a large range of ferromagnetic binary alloys. The sign of the interaction between d shells is taken to depend on whether the sum of their radii is greater or less than an arbitrarily chosen value. The values of the radii used are quite inaccurate (cf. Slater 1939, p. 349) and the errors may well be several times as large as the differences between adjacent tabulated values. Further, Carr assumes the sign of the interaction to be independent of the separation of the ions concerned, which seems very improbable for the range of alloys considered. Errors arising in these two ways will be particularly important just on either side of the critical value. Thus the basis for this table is very weak, and there is no theoretical reason for assigning the signs to the interactions in this particular way. It may be noted that the adoption of this table is contrary to Z (ii), and is therefore inconsistent with Zener's general prediction of antiferromagnetism in non-conductors.

Carr's treatment of the equilibrium conditions is mathematically incorrect. A rigorous solution of this problem shows that the conditions given by Carr for the applicability of his solutions are not sufficient, and that additional solutions (i.e. values of S_d, S_c etc. for equilibrium) may be obtained. Since the values of the parameters involved are not known, however, a quantitative comparison is not possible. It may also be shown that an equally adequate interpretation is provided using the table of interaction coefficients but without recourse to Z (iii).

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* To be referred to as Zener (I) and his other papers as Zener (II), Zener (III) and Zener (IV).

Neither Zener nor Carr consider the implication of their treatment on temperature dependent properties. Discarding Z (iii), Carr's model is similar to Néel's (1948) model of a ferrimagnetic, for which the inverse susceptibility $1/\chi$ depends hyperbolically on T. As indicated above, a detailed development of the model for Fe, Co, Ni may lead to a similar conclusion. Experimentally, Fe, Co and the alloys FeNi, NiCo, FeV show an almost linear relation between $1/\chi$ and T, and the slight curvature appearing in the curves for Ni and some NiCr, NiCo alloys receives a natural interpretation on the band scheme (cf. Wohlfarth 1949).

Thus without further modification Zener's treatment, quite apart from the lack of a firm theoretical basis, does not lead to agreement with experiment, and Carr's results cannot be considered as support for Zener's postulates.

I wish to express my thanks to Professor E. C. Stoner for guidance in this and other work, and to the Department of Scientific and Industrial Research for a grant.

Physics Department,
University of Leeds.
25th August 1952.

A. TEVIOTDALE.

CARR, W. J., 1952, *Phys. Rev.*, **85**, 590.
NÉEL, L., 1948, *Ann. Phys., Paris*, **3**, 137.
SLATER, J. C., 1939, *Introduction to Chemical Physics* (New York : McGraw-Hill).
WOHLFARTH, E. P., 1949, *Proc. Roy. Soc.* A, **195**, 434.
ZENER, C., 1951 I, *Phys. Rev.*, **81**, 440; 1951 II, *Ibid.*, **82**, 403; 1951 III, *Ibid.*, **83**, 299; 1952 IV, *Ibid.*, **85**, 324.

The Thermal Neutron Capture Cross Section of ^{84}Sr

When ^{84}Sr is irradiated in a nuclear pile, two radioactive isotopes are produced by neutron capture, ^{85}Sr and a metastable state $^{85\,\mathrm{m}}$Sr. From the work of Sunyar *et al.* (1952) it follows that 86% of $^{85\,\mathrm{m}}$Sr ($T=70$ min) decays by γ-emission to the ground state of ^{85}Sr ($T=65$ d), which in turn decays by K-capture and γ-emission (0·514 MeV) to stable ^{85}Rb. Thus if natural strontium is irradiated in a pile, measurements of the disintegration rate of the γ-activity due to ^{85}Sr and of the disintegration rate of the β-activity due to ^{89}Sr ($T=52{\cdot}5$ d) will enable the thermal neutron cross sections σ of ^{84}Sr and ^{88}Sr to be approximately compared.

We have recently been using pile-irradiated strontium in biological experiments in which the longer life γ-radiation from ^{85}Sr has been most useful in verifying the Sr content of various specimens. In the course of these experiments the two disintegration rates mentioned above were measured. A rough comparison of the isotopic cross sections did not appear to support the value of 100 barns* for σ^{84}Sr obtained by Pomerance and Arnette (1951). We decided therefore to compare these two cross sections more exactly.

'Specpure'† strontium carbonate was irradiated in the Harwell Pile and, after allowing two days for the shorter-life γ-activities of $^{85\,\mathrm{m}}$Sr and $^{87\,\mathrm{m}}$Sr ($T=2{\cdot}8$ h) to decay, the β-activity of a sample of the activated salt (~ 2 mg) was compared with that of a standard source of ^{32}P using a GM4 counter with a fixed geometry. It was confirmed that the γ-ray sensitivity of the counter was negligible, so that the γ-rays from the decay of ^{85}Sr did not affect the counting ratio which was determined to within 1%. Since the variation of sensitivity of the counter for β-particles of 1·5 and 1·7 MeV is very small, the disintegration rate of the ^{89}Sr in the counting sample could be calculated. Absorption tests were used to verify that there was no appreciable contamination of the β-particle emission from each source.

* Difficulty of estimating the purity of the samples of ^{84}Sr used produced large errors in this value. More recent estimation would indicate σ^{84}Sr to be <3 barns (Pomerance (1952), private communication).

† High purity 'Specpure' salts were obtained from Messrs. Johnson, Matthey and Co. Ltd.

The same sample was then placed in a fixed position in a scintillation counter using a thallium-activated sodium iodide crystal. The γ-ray activity of the sample was compared successively with that from a standard source of ^{131}I with a mixed γ-ray spectrum but predominantly of energy 0·36 MEV and ^{137}Cs (γ=0·663 MEV) supplied by the Isotopes Division at Harwell. The efficiency of the counter was thus interpolated for a γ-ray energy of 0·51 MEV, and so the disintegration rate of ^{85}Sr was obtained.

Accepting the value of 0·0050 barn for the isotopic capture cross section of ^{88}Sr (Seren *et al.* 1947), the value obtained for the isotopic capture cross section for ^{85}Sr was 0·32 barn ± 20%. As a test of the purity of the irradiated strontium salt, the β- and γ-ray activities were determined at various times over a month. The half-life of the β-activity was 52·5 days (^{89}Sr) and that of the γ-activity 67 days.

If the present value of σ is assigned to ^{84}Sr of relative abundance 0·55% the value of σ for the stable isotope ^{87}Sr can be calculated. Using the value of Colmer and Littler (1950) for the total capture cross section of natural Sr for thermal neutron (σ=1·35 barn) together with the value of 1·3 barn obtained for $^{87\,m}$Sr by Seren, Friedlander and Turkel (1947), the value of σ for ^{87}Sr is about 17 barns.

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Atomic Energy Research Establishment,
Harwell, Berks.
17th September 1952.

G. E. HARRISON.
F. D. SEYMOUR.

COLMER, F. C. W., and LITTLER, D. J., 1950, *Proc. Phys. Soc.* A, **63**, 1175.
POMERANCE, H., and ARNETTE, T., 1951, ORNL 1164, 20.
SEREN, L., FRIEDLANDER, H. N., and TURKEL, S. H., 1947, *Phys. Rev.*, **72**, 888.
SUNYAR, A. W., MIHELICH, J. W., SCHARFF-GOLDHABER, G., GOLDHABER, M., WALL, N. S., and DEUTSCH, M., 1952, *Phys. Rev.*, **86**, 1023.

The Origins of Background Tracks in Shielded Electron-Sensitive Emulsions

In a previous communication (Fremlin and Walters 1950) it was shown that a 200 μ Ilford G5 emulsion accumulated electron tracks at the rate of 31 ± 3 mm^{-2} per day when screened within 2-inch lead walls at a depth of 600 metres below ground. By the use of cleaner shielding it has been possible to reduce this background accumulation rate to 2·6 ± 0·1 mm^{-2} per day. This is considerably larger than the rate to be expected from cosmic radiation, which is estimated from the measurements of Miyazaki (1949) to be of the order of 10^{-2} mm^{-2} per day, and experiments have now been made to discover what proportion of the background arises from radioactive contamination of the plates themselves.

Origin of tracks	Observed rate of formation β (mm^{-2} per day)
Thorium present in glass backing	0·57 ± 0·05
^{40}K present in glass backing	1·00 ± 0·05
^{14}C present in gelatine	0·83 ± 0·06
Shielding (entering plate at upper surface)	0·14 ± 0·02
Total	2·54 ± 0·10
Total track density (separate count)	2·61 ± 0·09

As previously pointed out, the thorium and potassium contamination of the plate backing and the ^{14}C present in the emulsion layer may make an appreciable contribution to the background when external radiation has been reduced to a minimum. This has now been confirmed by an analysis of the spatial distribution in the emulsion layer of tracks formed during a two-month exposure. The analysis showed that a considerable proportion of the observed background arises from the glass backing, since the number of electron tracks intersecting the lower emulsion surface was found to be a factor of 2·4 greater than the number crossing the upper surface. The results of the analysis are shown in the table.

The thorium activity of the glass was estimated from the results of a count of α-particle tracks observed at the emulsion–glass interface, the difference between this and the total glass activity being ascribed to ^{40}K. The potassium content of the backing glass was found by analysis* to be 0·15%, while the activity quoted in the table is estimated to correspond to a concentration of 0·09%. ^{14}C present in the gelatine will produce tracks at the rate of $0{\cdot}76 \pm 0{\cdot}07$ mm^{-2} per day if present in the concentration of $0{\cdot}95 \times 10^{-12}$ g/g of carbon (Anderson and Libby 1947). In the table all low-energy tracks starting within the emulsion layer have been ascribed to the decay of ^{14}C.

The analysis indicates that the minimum background so far attained cannot be reduced by more than 10% with improved shielding if the normal G5 plate is used. A further reduction can, however, be achieved by coating the emulsion on to a support free from potassium and thorium. This has been verified using $\frac{1}{16}$-inch Perspex sheet as a backing. During a four-month exposure these plates accumulated tracks at the rate of only $0{\cdot}86 \pm 0{\cdot}11$ mm^{-2} per day in a 200 μ emulsion. This background may be attributed almost entirely to the ^{14}C present in the gelatine.

It is considered that the use of such plates for the detection of rare events such as double β-decay (Fremlin and Walters 1952) will enable the limiting half-life to be increased by as much as a factor of 10, since the comparatively short range of the tracks resulting from the decay of ^{14}C will, in many cases, permit them to be distinguished from the events under investigation.

The Physics Department,
University of Birmingham.
11th August 1952.

M. C. Walters.

Anderson, E. C., and Libby, W. F., 1947, *Phys. Rev.*, **72**, 931.
Fremlin, J. H., and Walters, M. C., 1950, *Proc. Phys. Soc.* A, **63**, 1178; 1952, *Ibid.*, **65**, 911.
Miyazaki, Y., 1949, *Phys. Rev.*, **76**, 1733.

* We are much indebted to Messrs. Chance for making this analysis.

REVIEWS OF BOOKS

Les machines à penser, by Louis Couffignal. Pp. 153. (Paris: Les Editions de Minuit, 1952.) No price given.

The author defines a thinking machine as a machine which can replace a human being in the performance of operations belonging to some class, however limited. Calculating machines clearly come into this category and their development is described beginning with the work of Pascal and ending with modern large-scale digital and analogue machines. Some comparisons are drawn between calculating machines and the cerebral cortex, both in relation to action and structure. This leads to a discussion of symbolic logic and ways of mechanizing it, and finally to a chapter on the problem of thought—but the net result is, as the author admits in a postscript, the statement of a series of questions to be answered by future research rather than a conclusion.

The author's approach to the problem of thought is to consider the brain as a machine which can derive systematically the consequences of propositions expressed in symbolic form and held in its memory, and which can store these consequences and use them as new data for a further series of deductions. He considers that the logical rules followed may not be the same as those of Aristotelian logic, and that light may be shed on them by a statistical examination of texts in a wide range of subjects in order to see what concepts are normally linked together. A diagram is given showing how certain logical processes can be carried out in a machine composed of elementary logical and storage elements. A comparison—which may perhaps strike some readers as a little naïve—is made between the connections in this machine and the arrangement of nerve fibres in the brain. The philosophical aspects of the subject are not embarked on.

The author appears to have been less influenced by a consideration of the properties of large universal calculating machines than have other writers who have stressed the ability of such machines to discriminate between different kinds of stimuli received through their input mechanisms and to modify their own programmes of instructions accordingly. In fact the amount of space devoted to universal calculating machines is sufficient for little more than a general description.

It would have been helpful if more references had been given to the sources on which the arguments are based, and if an index had been provided. Apart from this, however, the book is well written. M. V. WILKES.

An Introduction to Mathematical Physics, by R. A. HOUSTOUN. Pp. x+262. (London: Blackie, 1952.) 25*s*.

The familiar pre-war textbook of the same title which was first published in 1912 has been completely revised and extended in scope. In addition to chapters on attractions, hydrodynamics, heat conduction, wave motion, electromagnetic theory and thermodynamics, there are two new ones on quantum theory and relativity. As is to be expected in a book of this size, only the elementary parts of these subjects are included.

Where necessary, each topic is introduced by a short statement of the basic physical principles on which it rests, and, though these statements are rather over-simplified in places, they are in general sufficient introduction to the mathematical development which follows.

The reader is expected to have a fair knowledge of calculus, but the analysis required is derived at appropriate places in the text. Because of its extremely clear and straightforward presentation, the book will be of great assistance to physics students (for whom it was mainly written).

There are over 100 examples. Vector notation is not used. A. N. GORDON.

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Fouriersynthese von Kristallen und ihre Anwendung in der Chemie, by WERNER NOWACKI. (Lehrbücher und Monographien aus dem Gebiete der exakten Wissenschaften. Chemische Reihe, Band VI.) Pp. 237. (Basel: Verlag Birkhäuser, 1952.) 34.30 fr.

Professor Nowacki's book inevitably invites comparison with Dr. Booth's *Fourier Technique in X-ray Organic Structure Analysis.* Cursory examination of the tables of contents shows that the topics considered are almost identical, but there is a considerable difference in the approach. The difference does not quite reach that implied in the old story of the competition for the best book on the elephant, in which the English entry was entitled *Elephants I have Shot* and the German *Der Elefant als Grundbegriff in Philosophie und Metaphysik*, but the tendency is in that direction. Without intention of disparaging either book, it might be said that Dr. Booth is concerned with what he has himself found useful and Professor Nowacki with what might be useful to someone.

The first section (99 pages) is concerned with electron-density synthesis. Sixteen pages are devoted to explaining the use of Professor Lonsdale's structure-factor and electron-density formulae, with special reference to the space groups Pna (four pages) $P2_12_12_1$ (four pages) and $P2_1/c$ (two and one-half pages). Projections of the whole cell or parts of it are treated. There is considerable discussion of the effect of errors, both experimental and termination-of-series, and the various suggestions for avoiding them are described. The general tendency is to discourage the use of an artificial temperature factor as introducing greater errors and uncertainties than the 'diffraction' effects it is intended to remove. This conclusion might be anticipated from the known mathematical theorem that, of all finite trigonometrical series of given degree, the terminated Fourier series is the best mean-square approximation to the function to be represented. Other methods, such as continuing the series with calculated F's, are not subject to the same criticism. Methods of refinement (differential syntheses, least squares, steepest descents) are fully discussed, as well as methods of structure determination (trial and error, isomorphous replacement, heavy atom, algebraic methods, inequalities) and related questions such as the determination of absolute scale.

Patterson syntheses, including Harker and Buerger syntheses, occupy 78 pages. Dr. Booth devotes less than six pages to these topics, as " only on rare occasions have the Patterson or Patterson–Harker syntheses been of service ". The difference is partly due to Professor Nowacki's full discussion of space-group determination, based on Buerger's diffraction symbols. (Table 19, a more detailed version of these, is supplied as a separate booklet in a pocket of the cover. One wonders whether the convenience of this is outweighed by the risk of complete loss.) If enantimorphous pairs are counted as single space groups, x-ray (Laue) symmetry and absences alone are capable of resolving only 68 groups out of the total 219. Crystal class in addition would resolve all but eighteen groups, occurring in pairs. A detailed study of the heights and positions of the peaks in Patterson (or Harker or Buerger) syntheses would *in principle* resolve even these, but overlapping of maxima, which so often reduces the usefulness of Patterson syntheses, might make the resolution difficult in practice. The statistical methods of space-group resolution were developed too late for mention in Professor Nowacki's book; when applicable they would involve much less labour than the Patterson-synthesis methods.

The third and last section (46 pages) describes methods of numerical calculation, including several types of strips and analogue and digital computers. The use of strips appears to be given in sufficient detail to make reference to the papers of their originators unnecessary, but most of the computers are described only very briefly. Optical methods (' x-ray microscope ' and ' fly's eye ') are described in fair detail.

A few misprints were noted : a *nicht* seems to have been omitted in the definition of *gemischte Indizes* on p. 25, the bar over $\bar{h}$ is omitted (or has failed to print) in some places on p. 29, and $\mathbf{z}$ is printed for $\mathbf{y}$ on p. 144. The reviewer found a number of abbreviations (u.a., u.a.m., u.U., u.W., z.T.) puzzling, but they would presumably be clear to readers with a better knowledge of German. Still another meaning, this time $|F|^2$, is given to the expression ' structure factor '.

The book is highly recommended as a full, clear and detailed account of the matter within its field.

A. J. C. WILSON.

Nuclear Data, Supplement 3 (January 1951 to July 1951) to National Bureau of Standards Circular 499. Pp. 66. (Washington, D.C.: U.S. Department of Commerce, 1952.) Price $4.25 includes Circular 499 and three supplements.

A Guide to Tables of the Normal Probability Integral, National Bureau of Standards Applied Mathematics Series 21. Pp. iv+16. (Washington, D.C.: U.S. Department of Commerce, 1952.) 15 c.

Mass Spectrometry, Report of a Conference organized by The Institute of Petroleum. Pp. vi+205. (London: The Institute of Petroleum, 1952.) 30*s*.

CORRIGENDUM

A Theoretical Attempt to Predict the Excited States of Nuclei in the Neighbourhood of ^{208}*Pb*, by M. H. L. PRYCE (*Proc. Phys. Soc.* A, 1952, **65**, 773).

The statement (§ 6, p. 784) that the interaction energy of a hole and a particle has the same sign as for two particles is incorrect. The proper statement is that the interaction energy is given by the same formula as for two particles, provided ϵ_t and ϵ_s are replaced by $-\frac{1}{2}(\epsilon_t+\epsilon_s)$ and $\frac{1}{2}(\epsilon_s-3\epsilon_t)$ respectively. The conclusions regarding the doublet configuration in ^{208}Tl remain unaffected, but the order of levels in the quartet should be reversed. The agreement with the intensities of the alpha groups of ^{212}Bi is thereby spoilt.

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ABSTRACTS FOR SECTION B

X-Ray Analysis of Proteins, by W. L. Bragg.

ABSTRACT. The attempt to discover the atomic arrangement in the protein molecule seems very ambitious. Ever since Bernal first showed that crystals of protein gave x-ray diffraction pictures, it has been clear that a protein molecule of a given type is a structure with a definite individual form; the x-ray diffraction spots are very sharp and reproducible and extend to regions corresponding to interatomic distances. The molecules are, however, of great complexity. It has been a triumph of x-ray analysis to pass from simple substances like rock salt to such molecules as strychnine or penicillin with about one hundred atoms. We are now trying to analyse a molecule such as haemoglobin, which contains ten thousand atoms. The reward, if an analysis were completed, would be great, because the determination of any one protein would undoubtedly cast a flood of light on the character of these bodies, which Nature has selected as the basis of living matter.

Work on protein is going on in a number of centres. I wish to speak here in particular about the work on haemoglobin which has been going on in Cambridge for the last twelve years under the direction of Dr. Perutz. More x-ray data for haemoglobin are available than for any other protein. Though still a long way short of the goal, considerable advances have been made recently, so great as to encourage us to hope that the problem is soluble and even that a solution lies not far ahead.

The Dynamics of Small Transient Cavities, by W. D. Chesterman.

ABSTRACT. Experimental methods have been developed for creating and observing single spherical cavities in water and certain organic liquids. Rapid photography permits motion analysis to be made.

The cavities show several cycles of expansion and collapse during their lifetime of a few milliseconds. At each volume minimum a sharp pressure maximum occurs in the liquid.

It appears that these cavities form initially on minute gas nuclei in the liquids, and the existence of these nuclei is essential for the type of cavitation studied. The relation of cavity life to maximum diameter is discussed.

The Temperature Variation of the Magnetization of Nickel in Low and Moderate Fields, by R. S. TEBBLE, J. E. WOOD and J. J. FLORENTIN.

ABSTRACT. An account is given of measurements on the reversible changes in magnetization accompanying change in temperature in annealed nickel, and the results are discussed in relation to the work of Bates and others on the temperature changes produced by adiabatic changes in magnetization (the magneto-caloric effect). It is found that at relatively high fields, where the magneto-caloric effect is mainly reversible, the results are in good agreement with those obtained from direct magneto-caloric measurements, while for low field values a quantitative separation of the reversible and irreversible components of the magneto-caloric effect has been carried out. The result of an analysis of the reversible heating effect is compared with the estimate given in the theoretical investigation of Stoner and Rhodes, and it is suggested that, over the low field range considered, rotational processes predominate.

The Effect of Temperature of Deformation on the Electrical Resistivity of Cold-worked Metals and Alloys, by T. BROOM.

ABSTRACT. A special apparatus has been used to draw wires of various metals at temperatures between −183°c and 100°c, and to measure their resistances at the temperature of drawing. The change of resistivity with deformation was found to depend on the temperature of deformation relative to the recrystallization temperature. The results explain qualitatively the apparently anomalous resistivity increases previously reported for tungsten and molybdenum. It is suggested that a unified theory of the effect of deformation on the resistivity of both pure metals and alloys can be based on stacking faults.

Yield Points in Bending Experiments on Zinc Crystals, by M. J. DUMBLETON and B. W. HOWLETT.

ABSTRACT. It is shown that sharp yielding can be observed in previously unstrained zinc crystals by means of bending experiments devised to avoid premature overstraining of the specimen. This resolves a difficulty in the interpretation of previous tensile experiments on crystals which show the yield phenomenon.

Some Observations on the Yield Point in Zinc, by H. L. WAIN.

ABSTRACT. Evidence is given confirming that the yield point in zinc is due to nitrogen in solution. The theoretical prediction that a yield point should appear in a susceptible crystal without the necessity for any prior deformation is verified experimentally, and an explanation is given of the observation that a yield point may appear in a specimen even though free dislocations have been introduced subsequent to ageing.

Under certain conditions the yield point values in zinc decrease as identical strain-ageing treatments are repeated, and a smooth stress–strain curve is ultimately obtained. This is attributed to an accumulation of work hardening which causes the dislocation density to increase to such an extent that the dislocations can no longer be effectively anchored by the available nitrogen atoms. The difference between this behaviour and that of iron on repeated strain ageing is discussed.

A Critical Study of the Asymmetrical Temperature Gradient Thermoelectric Effect in Copper and Platinum, by N. FUSCHILLO.

ABSTRACT. A method is described by which metallic wires can be subjected to easily measurable but very pronounced asymmetrical temperature gradients without straining the wire. The electromotive forces developed by the application of symmetrical and asymmetrical gradients to annealed 'thermopure' platinum wire and specially prepared cables of copper wire, at both high and low temperatures, have been measured at many points along considerable lengths of wire. Precautions to minimize or eliminate spurious effects enabled measurements significant to $0{\cdot}01\ \mu$v to be taken.

The results provide no justification for the supposition that an asymmetrical temperature gradient thermoelectric effect exists, under the conditions of investigation, which cannot be explained in terms of inhomogeneity effects. The nature of these effects is discussed and some evidence is provided which indicates that the variation in the Thomson thermoelectric potential with strain and impurity is significant.